**US Army Corps
of Engineers**
Waterways Experiment
Station

*Installation Restoration Research Program*

# Laboratory Evaluation of a Volatile Organic Compound Analysis System for the Site Characterization and Analysis Penetrometer System

by   Karen F. Myers, James M. Brannon,
Richard A. Karn, Cynthia B. Price,
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Stafford S. Cooper

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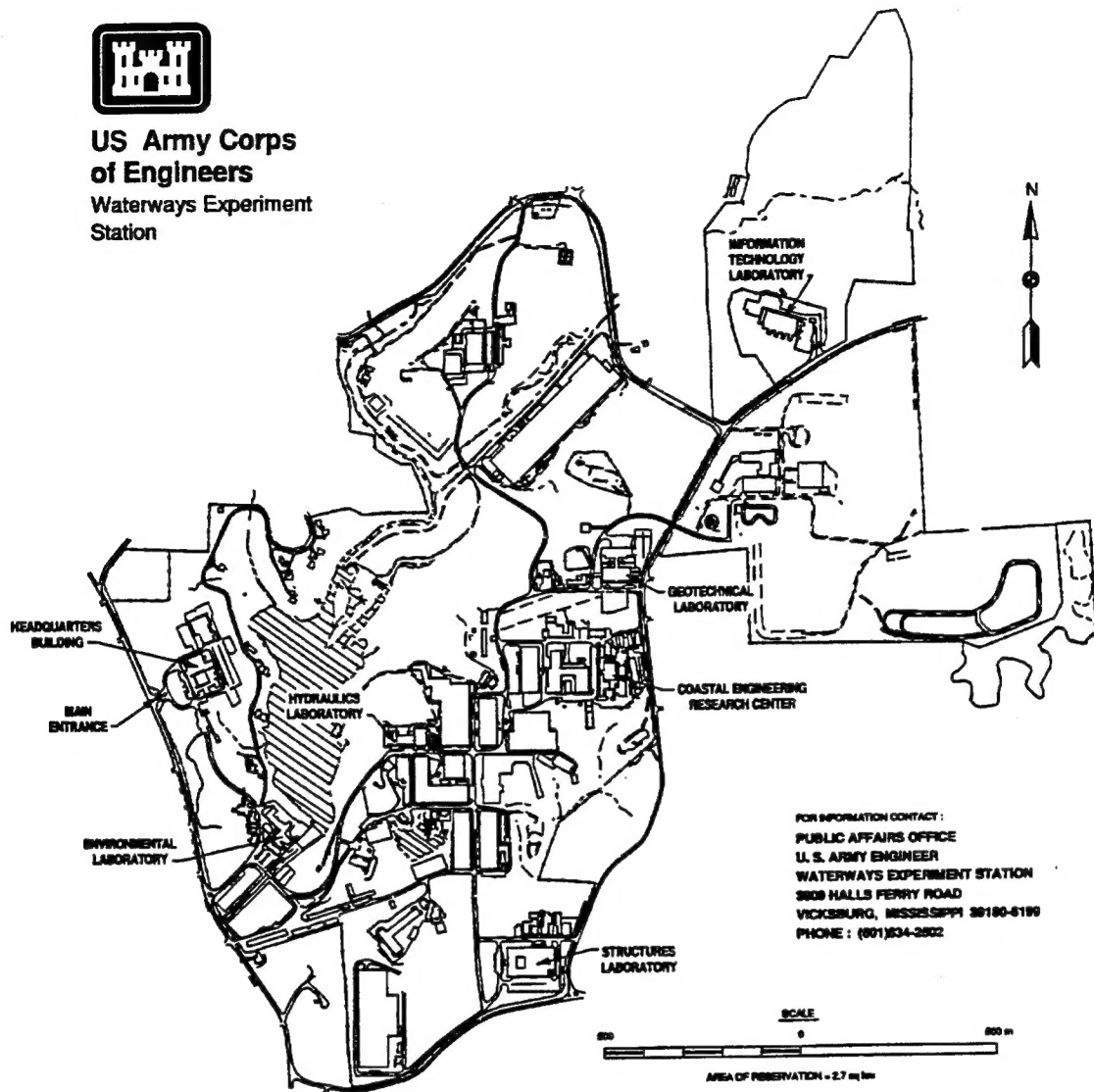     Dan Y. Eng, Ann B. Strong,
     Stafford S. Cooper

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     Waterways Experiment Station
     3909 Halls Ferry Road
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Final report

US Army Corps
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Waterways Experiment
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SCALE

AREA OF RESERVATION = 2.7 sq km

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# Preface

This report should be cited as follows:

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# 1    Introduction

## Background

The U.S. Department of Defense has become increasingly concerned with the environmental fate and remediation of the by-products of operating military installations. While emphasis has been placed upon cleanup of sites contaminated with explosive compounds, contamination also occurred during the normal operation of motor pools, machine shops, dry cleaning facilities, and other operations that routinely used organic solvents and fuel.

One of the first steps to remediation is identifying the type of contamination and delineating the size and shape of subsurface contamination. Conventional subsurface contaminant mapping technology requires laboratory analysis of soil samples taken from multiple borings across the site, operations that are time-consuming and expensive. High costs often preclude adequate descriptions of contaminant plumes.

Researchers at the U.S. Army Engineer Waterways Experiment Station (WES) developed the site characterization and analysis penetrometer system (SCAPS), a direct push sampling and analysis technology, as a means of offsetting some of the effort and cost involved in evaluating and delineating subsurface contaminant distributions. Current SCAPS fluorescence systems are capable of detecting polyaromatic organic compounds associated with petroleum, oils, and lubricants at contaminated sites. At present, a method for in situ detection of fuels and chlorinated solvents to compliment existing capabilities is unavailable. Researchers at WES have designed a volatile organic compound analysis system (VOC sampler) for the SCAPS program for onsite detection of low concentrations of volatile compounds.

The principle of thermal desorption used in gas chromatography for soil analysis was applied in the development of the VOC sampler. Volatilized compounds are transferred to the surface where they are trapped on an absorbent and later desorbed into a gas chromatograph (GC) for identification and quantitation. In operation, the probe will sample discrete volumes of soil, heat and desorb the volatile soil compounds, eject the spent sample, and then be pushed to successive depths where additional samples may be taken.

## Objective

An extensive laboratory evaluation was conducted to identify and correct design inadequacies and system limitations. The laboratory evaluation of the VOC sampler had the following four objectives: to determine the best tubing for transferring volatilized compounds to the surface; to measure transfer efficiency, target analyte recovery, temperature, sampling time, and baseline detection limits; to evaluate the effects of soil type on performance; and to test mechanical functioning and identify residual contamination, which included performance of the sample-collection device and the analytical instrumentation.

# 2 Experimentation

## Probe Description

The probe design consists of a series of steel cylinders with gas channels and piston chambers made tight by O rings (Figure 1). The central actuator rod is held in place by locking lugs during the closed position. The sample exit runs up the center of the actuator rod. The probe is pushed to sampling depth, the locking lugs are pneumatically released, and the piston is retracted to reveal the sample chamber (Figure 2). The sample chamber is heated by a nichrome-wrapped ceramic heater fitted with an inner, stainless steel protective sleeve and a thermocouple to monitor temperatures. The probe is then pushed an additional 3.81 to 4.45 cm to sample a plug of soil of a known diameter and an estimated volume (Figure 3). Carrier gas is introduced through the annular space between the outer housing and the actuator rod housing (Figure 4). The gas enters the sample chamber area through four equally spaced orifices above and behind the heater. It is preheated as it passes down the surface of the heating coil and into the bottom of the sample chamber where it sweeps upward over the soil plug to purge the VOCs as they are volatilized into the chamber. The gas carries the volatilized sample up through the sample exit line and into the sample collection device at the surface.

## Reagents

The laboratory evaluation included the BTEX compounds (benzene, toluene, ethylbenzene, and total xylenes) trichloroethene (TCE), and trans-1,2-dichlorethene (Table 1). These are the compounds most often found at sites contaminated by refueling, degreasing, and cleaning operations. The BTEX compounds are used as indicators for light-weight fuel spills. In addition to these target analytes, the analytical standard contained chlorobenzene; 1,2-dichlorobenzene (o-dichlorobenzene); 1,3-dichlorobenzene (m-dichlorobenzene); and 1,4-dichlorobenzene (p-dichlorobenzene). The dichlorobenzenes are of particular interest because they give an indication of how heavier, less volatile compounds will act within the VOC sampling system. TCE has historically been used as a degreasing solvent in motor pools and as a dry cleaning solvent. Trans-1,2-dichlorethene is a refrigerant and low-temperature chlorinated solvent and is also 1 of the 20 organic

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SAMPLE EXIT LINE

OUTER SAMPLER HOUSING

UPPER PISTON CHAMBER

ACTUATOR ROD

ACTUATOR ROD PISTON

LOWER PISTON CHAMBER

ACTUATOR ROD HOUSING

LOCKING LUG IN LOCK POSITION
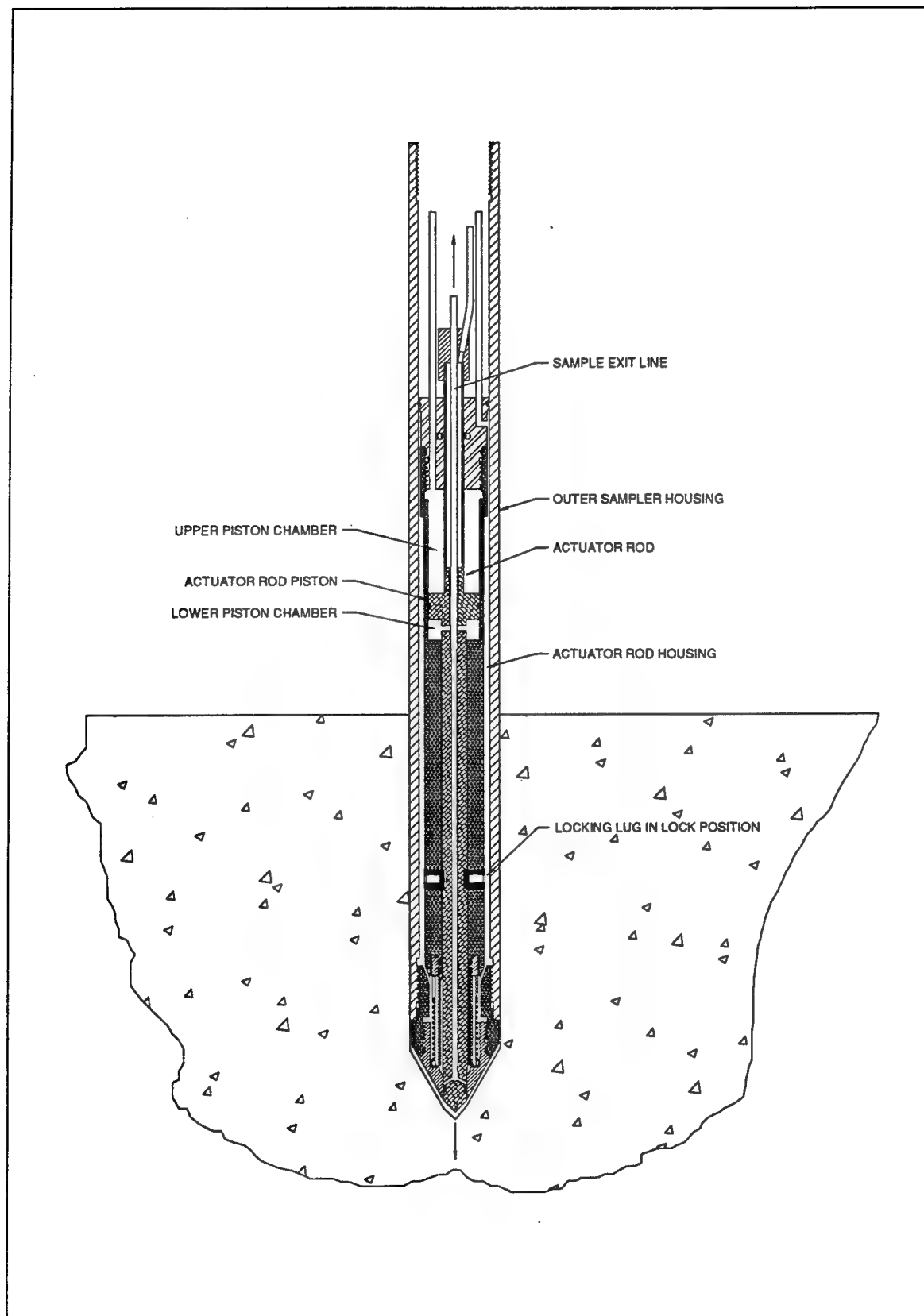
Figure 1.    VOC probe in push configuration

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ACTUATOR ROD PISTON

ACTUATOR ROD RETRACTED

LOCKING LUG IN RELEASE POSITION

CERAMIC HEATER

HEATING COIL

REMOVABLE STAINLESS STEEL
SAMPLE CHAMBER
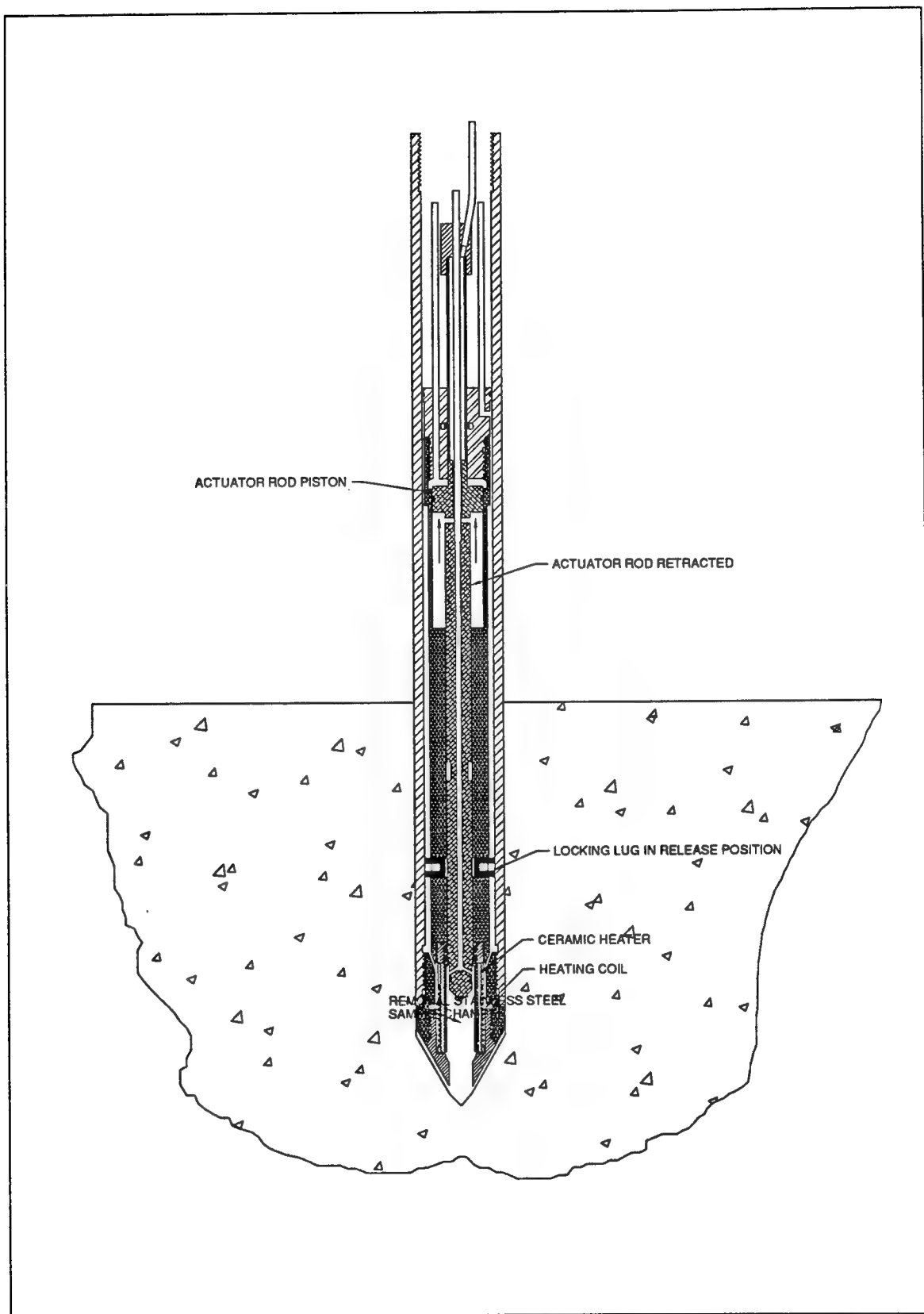
Figure 2.    VOC probe in ready-to-sample configuration

SAMPLE EXIT LINE

SOIL SAMPLE
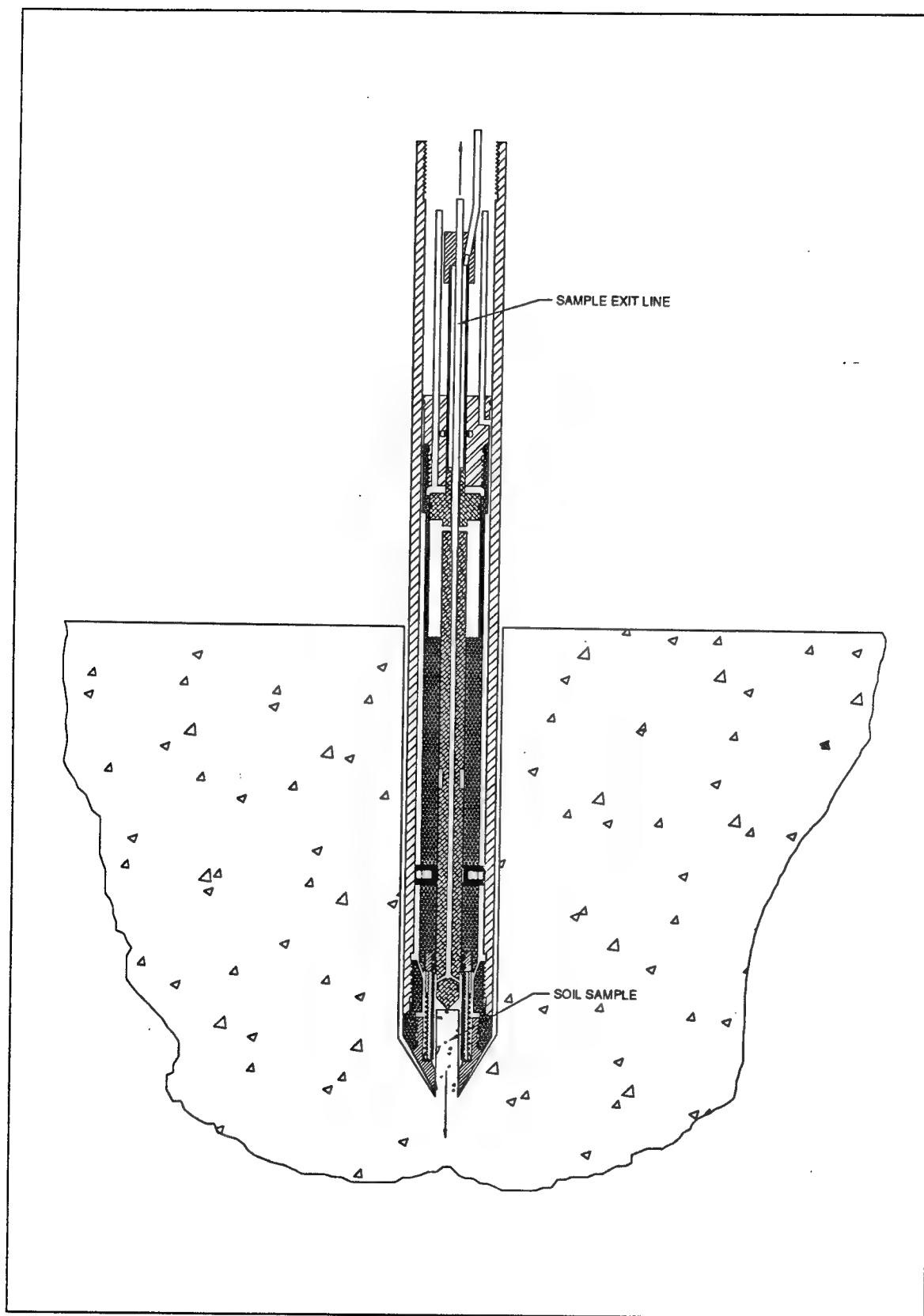
Figure 3.    VOC probe in sampling configuration
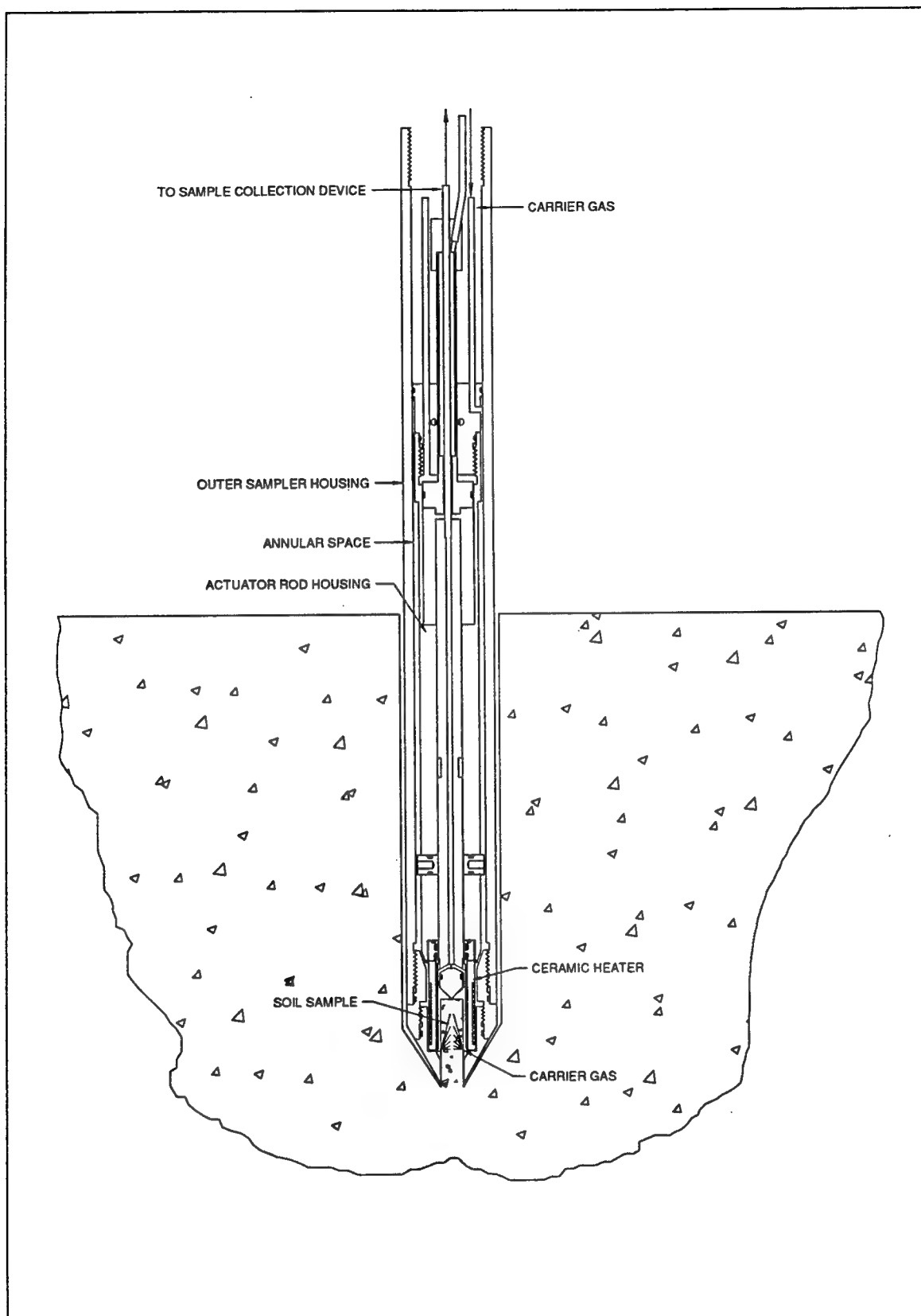
Figure 4. Carrier gas path during sampling

**Table 1**
**Physical Properties of Target Analytes**

| Name | MW | MP, °C | BP, °C | VP, kPa | SOL, mg/ℓ | $K_{ow}$ |
|------|-----|--------|--------|---------|-----------|----------|
| Trans-1,2-dichloroethene | 96.94 | -50 | 47.7 | 35.33 | 6,300 | 1.48 |
| Benzene | 78.12 | 5.5 | 80.1 | 10.13 | 1,790 | 2.13 |
| Trichloroethene | 131.39 | -73 | 86.7 | 8.0 | 1,370 | 2.29 |
| Toluene | 92.13 | -95 | 110.6 | 2.93 | 500 | 2.69 |
| Chlorobenzene | 112.56 | -45 | 131.7 | 1.17 | 500 | 2.84 |
| Ethylbenzene | 106.16 | -94.9 | 136.2 | 0.947 | 150 | 3.15 |
| o-Xylene | 106.17 | -25.2 | 144.4 | 0.666 | 170 | 3.12 |
| m-Xylene | 106.17 | -47.9 | 139.1 | 0.800 | 200 | 3.20 |
| p-Xylene | 106.17 | 13.3 | 138.35 | 0.866 | 160 | 3.15 |
| o-Dichlorobenzene | 147.01 | -17.0 | 180.5 | 0.133 | 150 | 3.38 |
| m-Dichlorobenzene | 147.01 | -24.7 | 173 | 0.252 | 110 | 3.38 |
| p-Dichlorobenzene | 147.01 | 53.1 | 174 | 0.080 | 80 | 3.39 |

Note:  MW = molecular weight; MP = melting point; BP = boiling point; VP = vapor pressure at 20 °C; SOL = water solubility at 15-25 °C; and $K_{ow}$ = octanol/water coefficient.

contaminants most frequently found in groundwater (Lucius et al. 1992). Trans-1,2-dichlorethene, which has the lowest boiling point of the compounds evaluated, gives an indication of how the more volatile compounds will behave in the system.

Spiking solutions were prepared in methanol (Burdick and Jackson) for purge and trap analysis from standard solution mixes.  BTEX mixes were obtained from AccuStandard.  TCE was obtained from NSI Environmental Solutions.  Standards solutions were prepared containing 10, 100, and 500 ng of each compound per microliter.  Spiked standard concentrations are reported in nanograms (ng) of mass of each compound.

Water was American Society for Testing and Materials (ASTM) Type I organic free prepared by passing water treated by reverse osmosis through a MilliQ UVPlus purification system.  Organic free water was used in the purge and trap system to generate standard curves and to moisten soil.  Organic residue grade hexane, acetone, and methylene chloride were used to clean the VOC probe.

# Instrumentation

A gas chromatograph/mass spectrometer (GC/MS) was used for the initial tube evaluation of target and tentatively identified compounds (TICs) and for the soil residue analysis. The system consisted of a Hewlett Packard 5890 series II gas chromatograph interfaced to a HP 5971 Series Mass Selective Detector with an OI Analytical model 4560 purge and trap. Traps for sample collection were packed with a mixture of tenax, silica gel, and charcoal. The analytical method was U.S. Environmental Protection Agency (USEPA) SW846 Method 8240 (1992a).

Most analyses were performed on the same analytical system that will accompany the VOC system to the field. The system consisted of a model 8610 portable GC (SRI Instruments, Las Vegas, NV) with a photoionization detector (PID) and electrochemical detector (ELCD) in series. Sample introduction was by purge and trap. The GC/PID was interfaced to a 486 computer with SRI Peaksimple II software for data analysis. The traps for sample collection were packed with tenax. The analytical method, modified from USEPA SW846 Method 8021A (1992b), used only the PID detector.

For analysis, the trap in the purge and trap sampler of both instruments was replaced with a trap containing the sample collected from the VOC sampler. This trap was desorbed and the analytes quantitated against a standard curve generated by the appropriate method.

# Methods

## Tubing evaluation

The VOC sampler thermally desorbs volatile compounds from soil and water, sweeping them to the surface in a gaseous state through a transfer line. In the laboratory evaluation, the length of the transfer line was limited to 50 ft. In the field, this is equivalent to the length of line required for a 20- to 25-ft push below ground surface (bgs). Previous field trials designed to test probe penetration depth indicate that 30 to 50 ft bgs is a reasonable expectation for a probe the diameter of the VOC sampler (Lee et al. 1994). Sampling depth was simulated by using two lengths of coiled tubing, a carrier gas inlet, and a sample exit, each 50 ft long. Various types of tubing having different physical characteristics were tested (Table 2).

Because many of the BTEX compounds are used as solvents in manufacturing, each tube was tested, prior to its use in the system, for residues of these solvents as well as other volatile compounds that could cause analytical interferences. A 50-ft section of tubing representing the sample transfer line was attached to a helium source fitted with an off/on valve and a stainless steel swagelok metering valve in series. The metering valve was adjusted to deliver a stream of gas between 35 and 40 ml/min. The opposite end of the tube was

**Table 2**
**Types of Tubing Evaluated and Their Physical Properties**

| Tubing | Length, m | OD, cm | ID, cm | Volume, $cm^3$ | Maximum Temperature, °C |
|---|---|---|---|---|---|
| Viton | 15.2 | 0.64 | 0.32 | 120.7 | 260 |
| Nylon | 15.2 | 0.32 | 0.20 | 46.98 | 65 |
| Fused Silica Capillary | 15.0 | – | 0.053 | 0.0331 | 300 |
| Teflon PTFE | 15.2 | 0.30 | 0.15 | 52.78 | 240 |
| Tefzel | 15.2 | 0.32 | 0.24 | 66.79 | 150 |
| 1/16-in. Stainless Steel premium grade 304 | 15.2 | 0.16 | 0.076 | 6.97 | -- |
| Nickel SP-Alloy (T-1) | 15.2 | 0.32 | 0.21 | 52.78 | – |
| PEEK | 15.2 | 0.32 | 0.16 | 29.68 | 160[1] |

[1]  Heat distortion temperature:  can withstand temps up to 250 °C.

attached to a second swagelok metering valve.  This valve, along with the off/ on valve, was used to isolate the system during tests.  The coil of tubing was wrapped with 120-volt heating tape and heated to 70 ± 5 °C with gas flow for 2 hr prior to sampling.  Preliminary tests indicated that heating was required to reduce the potential for analyte condensation along the 50 ft of transfer line after the heated gas stream exited the probe.  The test sample was collected on a trap attached to the second metering valve.  Samples were collected by passing the stream of gas through the heated tube and into the trap for 60 min.  These samples were analyzed for VOCs and TICs by GC/MS.

Each type of tubing was evaluated for spike recovery and elution profile (the time required to elute each compound).  Two 50-ft sections of tubing were used for this test.  The first 50-ft tube, representing the carrier gas inlet line, was attached to a helium source at one end and to an injection port made from a stainless steel swagelok T fitted with a GC septum at the other.  The second tube, the sample exit transfer line, was attached to the other end of the swagelok T injection port.  A second metering valve was fitted to the end of this line.  During timed tests, flow through the system could be stopped using the on/off valve at the regulator and the second metering valve as was described above.  Flow through the system was adjusted to 35 to 40 ml/min and in subsequent tests, to 55 to 60 ml/min for selected tubing.  For spiked tests, the tubing was flushed for 2 hr before sampling began.  During the initial tests, neither the tubing nor injection port were heated to determine the worst case recovery scenario.  A trap suitable for the SRI GC was attached in line and a blank sample was collected for 1 hr.  The blank trap was removed and a second trap attached.  A standard containing 500 ng of each compound was injected directly into the system.  At timed intervals over 1 to 2 hr, flow through the system was stopped between the two valves, and traps were

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exchanged to establish compound elution profiles. Total recoveries were summed from traps collected during each sampling period. A control was taken by attaching a trap directly onto the injection port.

## VOC system evaluation

To evaluate the VOC system, the two 50-ft sections of transfer line were attached to the probe. While the tubing forming the sample exit transfer line varied with each test, the carrier gas inlet line was tefzel for all tests. The actuator rod was retracted into the probe, forming the sample chamber. The opening was fitted with an expandable plug designed to seal the base of the chamber. Then the entire system was tested for gas tightness. The system was fitted with metering valves used to control gas flow and isolate the system.

Heater temperature was set at either 70 or $100 \pm 5$ °C; tube temperature was either ambient room temperature or 70 °C. Gas flow was 35 to 40 ml/min and 60 ml/min. Samples were collected on traps at timed intervals and analyzed by GC/PID.

## Effects of soil type

VOC sampler system performance was tested against three standard soils: Ottawa sand, Vicksburg loess (silt), and buckshot clay. Dry, 2-mm-sieved soil was mixed with organic free water to simulate moisture contents by weight of 10 and 20 percent (silt only). Prepared in this way, the soils had no free standing water and were of a uniform consistency that packed and held together well. Soil was packed into a 500-ml stainless steel beaker 1/2 in. at a time to a depth of 3 in. to obtain a weight density of 1.7 $g/cm^3$. For sampling, the VOC probe was held upright in a rack with the opening plugged. The probe was heated and gas flow was established. After purging, a system blank was taken over a period of 60 min (labeled B60). The sealing plug was removed and the gas flow was stopped. The soil, which was placed on a hydraulic jack, was raised 4.45 cm, forcing the soil into the probe's sample chamber. The beaker was slowly removed leaving a plug of soil in the sample chamber. The opening was quickly sealed with a Teflon-coated septum held in place by a notched, stainless steel support. The septum support was held against the probe opening with a jack offset 6 in. from the probe. A total of 1,000 ng of each compound was injected into the center of the soil sample. The flow was reestablished, and a minimum of three additional traps were collected per sample over a period of 2 hr. The primary sample was collected during the first 30 min (T30), after which the soil was ejected and the trap changed. A second trap, representing the analyte residue remaining in the system after soil ejection, was collected for 30 min (T60). The third trap, collected for an additional hour (T120), represents the background analyte residue carryover between samples. After sampling, the soil plug was analyzed for percent moisture or for residual target compounds by GC/MS. Soil

weight was measured by weighing the beaker before and after the soil sample was taken.

## Evaluation of probe contamination and mechanical functioning

Contamination of the probe and gas manifold was evaluated by sweeping helium through the sample path and trapping the gas for 60 min. The heater inside the probe was calibrated by comparing the temperature of the thermocouple to the temperature of the center of the sealed sample chamber with gas flowing. Gas tightness was tested by measuring gas flow entering and leaving the probe. In addition, a Matheson Leak Hunter, Model 8065, was used to check the entire VOC sampler system for leaks throughout the study. Mechanical functioning of the piston and locking lugs was tested by repetitively actuating the pistons and monitoring system performance. O ring failure was detected by mechanical system failure or gas leakage.

# 3 Results and Discussion

## Tubing Evaluation

Eight types of tubing were evaluated for their physical and chemical characteristics as possibilities for the sample transfer line (Table 2). The criteria were as follows: the amount and types of residual contamination remaining from the manufacturing process; the transfer efficiency of target analytes through the tubing; and strength, flexibility, size, and operating temperature of the tubing.

In order to function properly, transfer lines must be rugged enough to withstand the physical stresses of being flexed and coiled repeatedly. Four transfer lines are connected to the top of the VOC probe (Figure 5). Lines 1 and 2 supply gas to operate the actuator rod. Line 3 supplies gas to operate the locking lugs and also serves as the inlet carrier gas supply for the sampler. The fourth line is the outlet for the volatilized sample and afterward allows the gas flow to be reversed in order to pressurize the sample chamber and help eject the soil plug. Lines 1 and 4 are attached to the actuator rod. These lines must move up and down 4.45 cm as the rod opens and closes the sampling port. During operation, all tubing and wires are wrapped together in heat shrink plastic to form an umbilical line between the VOC probe and the SCAPs truck. The umbilical is threaded through sections of 1-m-long push pipe that are 5.08 cm in diameter. The inner diameter is approximately 4.45 cm. During storage, these pipes are stacked alternately on racks about 0.3 m apart, forcing the umbilical into a repetitive S shape with an arc length of approximately 0.4 m extending from either end and connecting each section of pipe to the next section. Any tube used for the transfer lines must be strong enough and flexible enough to withstand the bending and straightening of stacking and unstacking the push pipes without breaking or kinking. It must also be small enough to allow the umbilical formed to move freely through the pipes. In addition, the inner diameter of the tube must be large enough to provide an adequate volume of gas to help eject the soil plug.
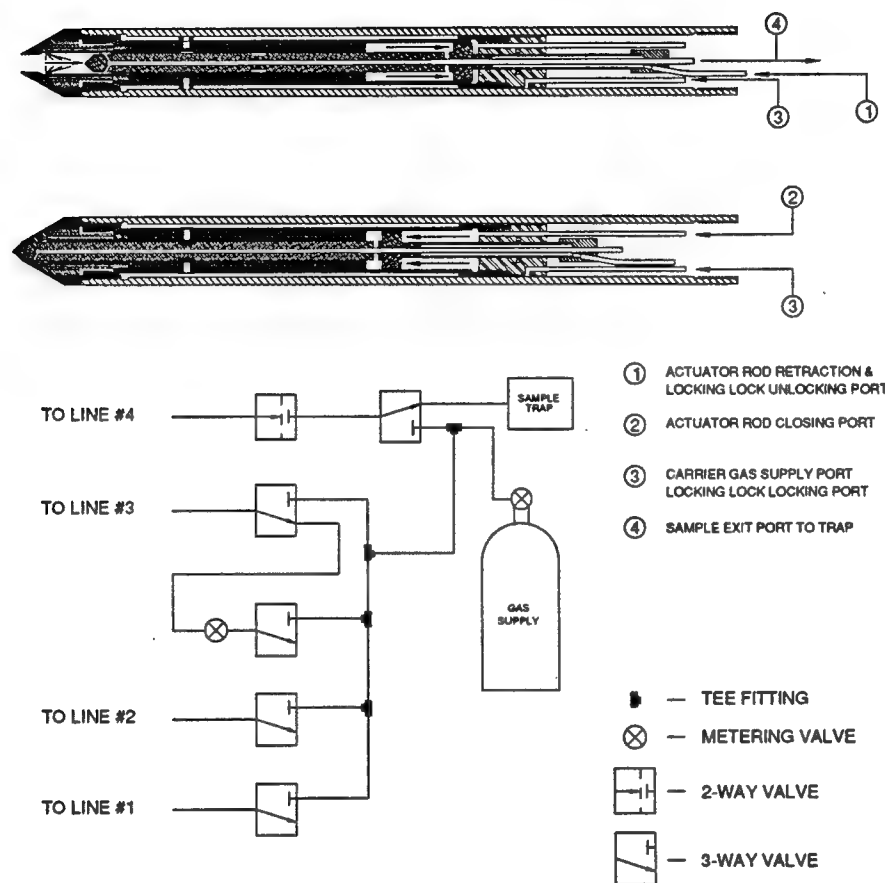
Figure 5.    VOC probe pneumatic and gas supply schematic

## Ruggedness

Of the types of tubing evaluated, viton (polyvinylidenefluoride hexafluoro-propylene), with an outer diameter of 0.64 cm, would form the largest diameter umbilical if used for all four transfer lines. The nylon tubing evaluated was also a fairly large diameter tube, but, while flexible enough to be considered, its maximum operating temperature is only 65 °C. The Nickel SP-Alloy, the least flexible tubing tested, was eliminated because it could not easily accommodate the bending required. The 1/16-in. stainless steel is the type of tubing routinely used for high performance liquid chromatography (HPLC). It is flexible enough to allow the required bending and straightening, but would have to be guided into form manually. It has the second smallest inner diameter of the tubing tested and does not transmit sufficient force into the sample chamber to eject the soil plug. The fused silica capillary is a fairly strong material. It will bend and unbend easily and should resist breakage if handled carefully. The weakest points are the connections to the probe and to the manifold. This tubing will not provide the volume of gas required to operate the probe, however, and could only be considered for use as the sample outlet if the system were redesigned to eject the soil without the aid of gas directed down the sample outlet transfer line.

Teflon, tefzel, and PEEK (polyetheretherketone) were flexible enough to meet the physical requirements of the transfer lines and small enough in diameter to form an acceptably sized umbilical. The added strength provided by binding the four lines into the umbilical offered considerable protection from bending or kinking during use. All three also provided sufficient gas force to eject the soil plug.

## Manufacturing contamination

Low levels of organic contamination resulting from tubing manufacture were found in all tubing when testing first began (Table 3). The presence of toluene in most of the tubes suggests laboratory contamination. As tests progressed for selected tubing, contamination was reduced to acceptable levels of less than 2.1 µg/ℓ of carrier gas per hour of sampling. This suggests that a period of conditioning is necessary before a new set of transfer lines supplying carrier gas to and from the VOC sampling chamber are put into service. A review of the TICs (Appendix A) shows that PEEK, tefzel, and viton suffer the most from release of nontarget compounds. The remaining tubing showed traces of alkanes, aldehydes, ketones, and dichlorobenzene.

For tubing selected for further testing by GC/PID, the first blank of the test series was used to detect contaminants. Tests were performed at 25, 70, and 100 °C. Not all compounds detected by GC/MS were visible to the GC/PID. The PID detector uses an HNU-type 10.2 electron volt lamp capable of detecting compounds with an electron potential of 10.2 electron volts or less. This compound selectivity is the reason the PID is the detector of choice for BTEX analysis. Although the PID can detect many chlorinated compounds, the

**Table 3**
**Tube Manufacturing Contaminants Determined by GC/MS—Method 8240**

| Target Compound | Control | Viton | Nylon | Capillary | Teflon | Tefzel | Stainless | Nickel | PEEK |
|---|---|---|---|---|---|---|---|---|---|
| Trans-1,2-dichloroethene | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 |
| Benzene | <2.1 | 8.3 | 0.8 | <2.1 | <2.1 | 5 | <2.1 | <2.1 | 5.8 |
| Trichloroethene | <2.1 | 0.8 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 |
| Toluene | 0.4 | 20 | 4.2 | 0.8 | 1.7 | 3.3 | 0.4 | 1.2 | 0.8 |
| Chlorobenzene | <2.1 | 2.5 | 0.8 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 | <2.1 |
| Ethylbenzene | <2.1 | 2.5 | 0.4 | <2.1 | 0.4 | <2.1 | <2.1 | <2.1 | <2.1 |
| Total Xylenes | <2.1 | 14.2 | 2.9 | <2.1 | 2.1 | <2.1 | <2.1 | <2.1 | 0.4 |

Note: Tubes were heated at 70 °C with 35- to 40-ml/min flow for 2 hr. Concentrations are in micrograms per liter of gas and are based upon 1 hr of sampling.

fluorinated compounds listed in the TICs analysis for tefzel were invisible to it. Analysis of both unheated and heated tefzel and 1/16-in. stainless steel tubing resulted in a clean baseline by GC/PID with background levels equivalent to less than 5 ng/g (5 ppb) in soil. Contaminant peaks were from methylene chloride and from acetone, possibly the result of laboratory contamination. Neither peak eluted at the same time as any of the target compounds. Heated PEEK tubing emitted volatile compounds that were clearly visible to the PID detector. These compounds caused interferences across the entire chromatogram. Some eluted very close to target compounds, and some were confirmed as the target compound. After several days of heating, contaminant levels were reduced enough to make the tubing usable. For field use, PEEK tubing will have to be pretreated and tested to ensure that contaminants are removed. After several hours of heating, the PEEK tubing began to mold and harden into shape. While none of the experiments involved heating PEEK over 100 °C, longer transfer lines and sampling for less volatile compounds might require increased transfer line temperatures. The heat distortion temperature for PEEK is reported to be 160 °C; however, prolonged use at temperatures greater than 100 °C could also cause the tubing to become less flexible and more prone to breakage.

## Compound recovery

For all tubing tested at ambient temperature, trans-1,2-dichloroethene, the most volatile compound, yielded recoveries less than 20 percent (Tables 4 and 5). Recoveries improved slightly when a second trap was added in series with the first trap (whether it was sampled after 15 min or 30 min) (Figure 6). This demonstrated that tenax is not the appropriate trap for the most volatile compounds. The GC manufacturer suggests using a mixed trapping material or one such as Carbosieve for these compounds.

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**Table 4**
**Percent Recoveries (standard error) From 500-ng Spikes After 30 min of Sampling (GC Method 8021A) From the Tube Evaluation Tests**

| Target Compound | Control | Viton | Nylon | Capillary | Teflon | Tefzel | Stainless | PEEK |
|---|---|---|---|---|---|---|---|---|
| Trans-1,2-dichloroethene | 0.0 (0.0) | 16.3 (8.2) | 0.0 (0.0) | 2.0 (0.1) | 6.4 (0.1) | 6.9 (1.3) | 3.1 (2.2) | 9.5 (10.9) |
| Benzene | 97.9 (0.5) | 75.7 (3.7) | 103 (1.1) | 106 (2.5) | 101 (1.8) | 107 (1.8) | 106 (2.7) | 102 (3.6) |
| Trichloroethene | 96.3 (0.9) | 76.5 (8.4) | 97.0 (7.8) | 105 (4.0) | 94.6 (3.5) | 101 (1.4) | 105 (2.6) | 102 (4.0) |
| Toluene | 95.9 (3.8) | 41.1 (1.9) | 102 (8.6) | 107 (2.1) | 99.1 (1.7) | 93.1 (0.4) | 105 (2.4) | 97.4 (3.1) |
| Chlorobenzene | 97.5 (4.0) | 14.6 (1.0) | 80.0 (4.3) | 107 (2.2) | 93.2 (1.9) | 84.7 (1.8) | 95.7 (1.9) | 95.4 (3.1) |
| Ethylbenzene | 94.3 (1.3) | 24.4 (1.0) | 101 (7.2) | 101 (2.4) | 94.2 (3.0) | 84.7 (1.3) | 102 (5.3) | 94.7 (3.2) |
| *m*- and *p*-Xylenes | 100 (12.7) | 10.3 (1.0) | 91.2 (3.7) | 112 (5.9) | 89.3 (9.6) | 93.8 (4.6) | 97.0 (1.3) | 102 (7.7) |
| *o*-Xylene | 98.3 (3.1) | 8.3 (0.6) | 89.6 (1.9) | 108 (2.4) | 93.1 (2.7) | 87.0 (1.6) | 99.8 (1.5) | 97.3 (1.0) |
| *m*- and *p*-Dichlorobenzene | 100 (4.6) | 3.5 (2.4) | 29.1 (21.5) | 110 (7.2) | 55.7 (4.2) | 37.4 (1.3) | 90.7 (7.6) | 86.0 (4.5) |
| *o*-Dichlorobenzene | 103 (2.2) | 2.1 (1.3) | 24.6 (10.0) | 108 (2.8) | 65.1 (1.2) | 43.9 (1.2) | 93.0 (12.2) | 87.8 (1.4) |

Note: Tube temperature was 25 °C with a flow rate of 35 to 40 ml/min.

**Table 5**
**Percent Recoveries (standard error) From 500-ng Spikes After 60 min of Sampling (GC Method 8021A) From the Tube Evaluation Tests**

| Target Compound | Control | Viton | Nylon | Capillary | Teflon | Tefzel | Stainless | PEEK |
|---|---|---|---|---|---|---|---|---|
| Trans-1,2-dichloroethene[1] | 11.0 (0.6) | 25.4 (1.5) | 44.2 (10.6) | 55.2 (16.7) | 59.5 (8.8) | 50.8 (6.0) | 73.9 (28.6) | 33.0 (9.2) |
| Benzene | 97.9 (0.5) | 84.0 (4.1) | 103 (1.1) | 106 (2.5) | 102 (1.4) | 114 (2.4) | 107 (2.4) | 102 (3.6) |
| Trichloroethene | 96.3 (0.9) | 84.6 (8.6) | 97.0 (7.8) | 105 (4.0) | 96.9 (2.8) | 104 (1.2) | 105 (2.6) | 102 (4.0) |
| Toluene | 95.9 (3.8) | 60.0 (3.6) | 102 (8.6) | 107 (2.1) | 101 (2.1) | 97.3 (0.3) | 106 (1.1) | 97.4 (3.1) |
| Chlorobenzene | 97.5 (4.0) | 36.4 (2.5) | 80.0 (4.3) | 107 (2.2) | 97.0 (2.6) | 92.8 (1.6) | 96.4 (1.8) | 97.2 (3.4) |
| Ethylbenzene | 94.3 (1.3) | 47.1 (3.4) | 101 (7.2) | 101 (2.4) | 97.5 (1.3) | 90.1 (1.4) | 102 (5.3) | 94.7 (3.2) |
| *m*- and *p*-Xylenes | 100 (6.3) | 32.5 (1.6) | 91.2 (1.9) | 112 (3.0) | 93.3 (7.1) | 100 (2.0) | 98.0 (0.6) | 103 (4.1) |
| *o*-Xylene | 98.3 (3.1) | 27.2 (1.6) | 89.6 (1.9) | 108 (2.4) | 96.6 (4.8) | 93.3 (1.4) | 101 (0.6) | 97.8 (1.0) |
| *m*- and *p*-Dichlorobenzene | 100 (1.7) | 8.4 (2.9) | 32.7 (11.0) | 112 (3.9) | 67.8 (9.0) | 61.5 (2.0) | 98.2 (6.2) | 92.6 (1.9) |
| *o*-Dichlorobenzene | 103 (2.2) | 3.8 (2.3) | 27.9 (10.3) | 109 (2.5) | 74.4 (5.6) | 64.6 (2.1) | 95.0 (3.5) | 92.3 (1.2) |

Note: Tube temperature was 25 °C with a flow rate of 35 to 40 ml/min.
[1] Percent recovery includes concentration of analyte recovered from a second trap attached in series to the primary trap.
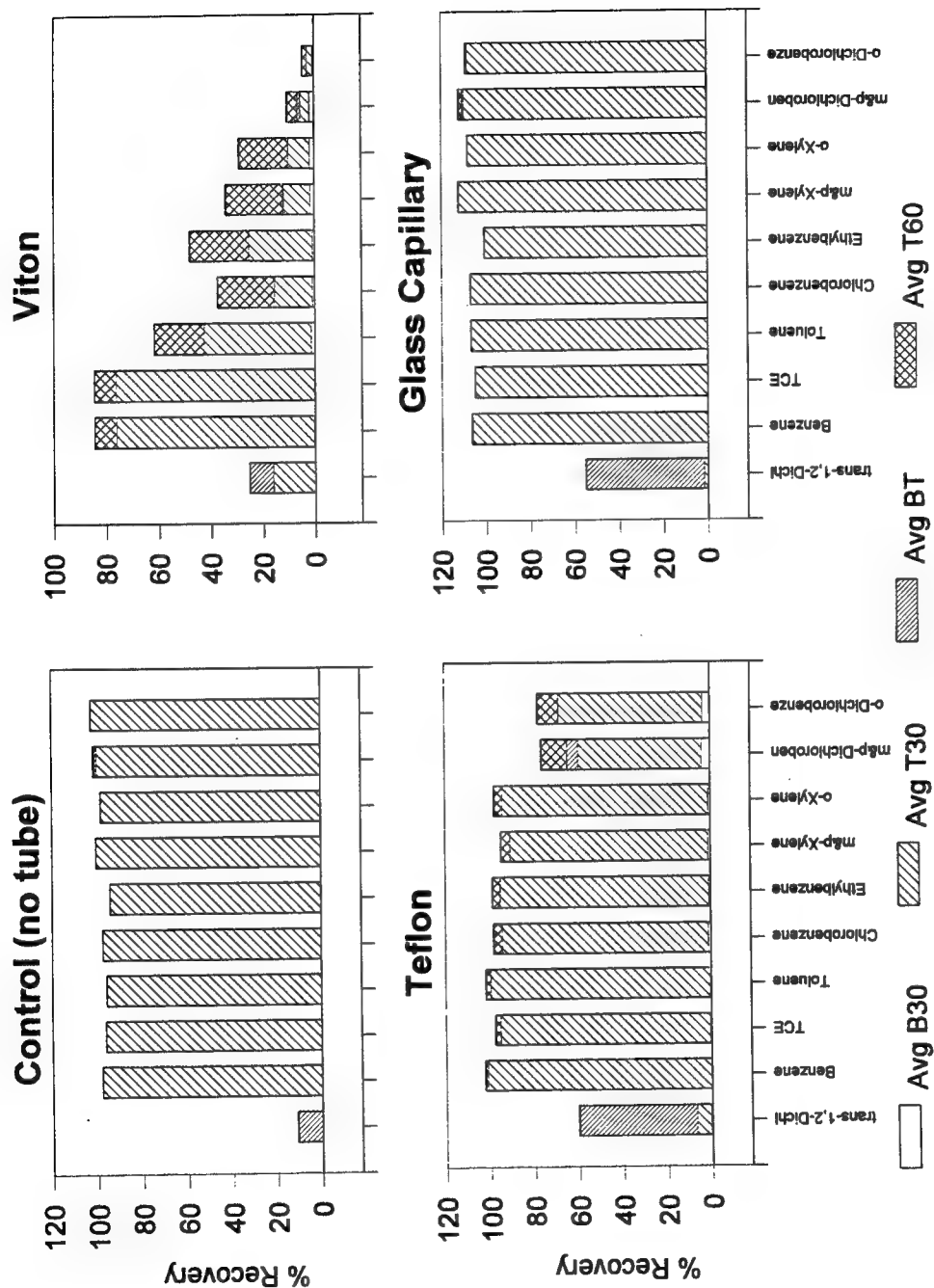
Figure 6. Average percent recoveries of VOCs with various types of tubing (Continued)

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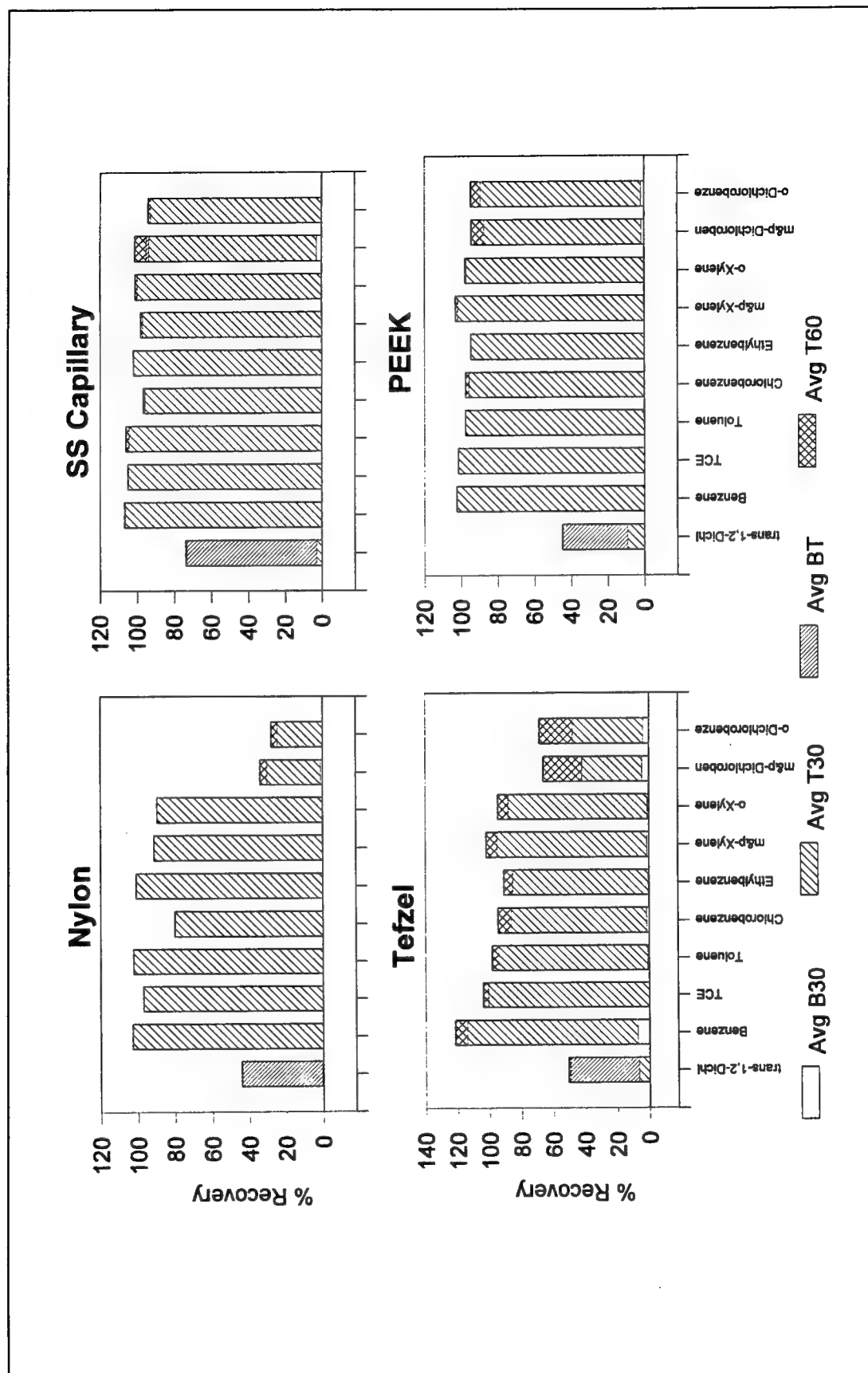
Figure 6. (Concluded)

Recovery depends upon several factors that cause the tubing to act like a long chromatographic column. The analytes move through at different rates depending on molecular weight, polarity, functional groups, and the volume and reactivity of the tubing traversed. The fused silica capillary and the 1/16-in. stainless steel tubing have the smallest tube volumes (Table 2) and are made of inert materials that do not react with the analytes. With the exception of trans-1,2-dichloroethene, recoveries for both tubings were nearly 100 percent for all analytes tested.

Viton has a much larger volume, 120.7 $cm^3$ per 50 ft. After 30 min of sampling, only two compounds, benzene and TCE, exhibited recoveries greater than 50 percent. After 60 min, only one additional compound, toluene, exhibited greater than 50-percent recovery. The heaviest BTEX compounds, the xylenes, showed less than 35-percent recovery. The dichlorobenzene compounds exhibited recoveries of less than 10 percent. Viton was eliminated from further testing because of poor recovery, large tube diameter, and target compound contamination.

Nylon, another polymer, showed maximum recoveries of 90 percent or better for the BTEX compounds and TCE after 30 min of sampling. Chlorobenzene recovery was 80 percent. Recoveries of the dichlorobenzenes were less than 30 percent. After 60 min, recoveries of the dichlorobenzenes had improved, indicating that they were moving slowly through the tubing.

Average recoveries after 30 min for Teflon were approximately 90 percent or better for all analytes except the dichlorobenzenes, which were less than 70 percent. Recoveries for benzene, TCE, toluene, and xylene were similar in the tefzel tubing. Recoveries of chlorobenzene, ethylbenzene, and dichlorobenzene were poorer. Recoveries of compounds in both tubes improved after 60 min, suggesting that traces of the more volatile compounds and greater amounts of the less volatile compounds remained in the tubing after 30 min. Dichlorobenzene recovery from both tubes ranged between 60 and 75 percent after 60 min. A comparison of recoveries for chlorobenzene, ethylbenzene, and the dichlorobenzenes suggests that tefzel has a greater chromatographic effect on these compounds than does Teflon.

After 30 min of sampling, the PEEK tubing showed average analyte recoveries greater than 94 percent for all compounds except the dichlorobenzenes. Dichlorobenzene recoveries were greater than 85 percent after 30 min and greater than 92 percent after 60 min. Fifty feet of PEEK tubing has a volume of 29.7 $cm^3$, the third smallest volume of tubing evaluated. Tests indicate that the tubing did not react with chlorobenzene and yielded acceptable recoveries within a 30-min sampling time.

While no one tubing stood out above the others as a best choice for the heated sample transfer line, three tubings were selected for further testing: tefzel, 1/16-in. stainless steel, and PEEK. All three tubings are flexible, chemical resistant, and exhibited BTEX recoveries greater than 85 percent in unheated transfer lines.

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## Optimization of sampling temperature and flow

Tests indicated that 30 min is a reasonable sampling time. Movement of the less volatile analytes through the transfer line could be improved by either increasing the gas flow or by heating the line to reduce analyte condensation along the length of the tubing. Additional tests were performed on the tefzel and stainless steel to evaluate the effects of temperature and gas flow on the rate of analyte recovery. In these tests, the tubing was placed in an oven with the injection port and trap external to the oven. One of the first questions to be answered was whether high temperature and increased flow would affect trap analyte recovery. To answer this, a second trap was attached in series, increasing the effective length of the trapping system. The second trap would capture any analyte that might either pass through the first trap or break through if the heated gas began desorbing analytes from the tenax.

Preliminary results using tefzel heated to 70 and 100 °C showed elevated recoveries for all of the compounds (Table 6). Although the experiment did not answer the original question, it did reveal another important consideration when choosing a material for a heated transfer line, permeation. Fluoropolymers such as Teflon and tefzel have been demonstrated to be permeable to gases (Kjeldsen 1993). In this test, the oven had been used to dry soils and had become contaminated. Volatile compounds in the oven penetrated the tefzel polymer and moved through the transfer line into the carrier gas stream where they caused significant contamination to the sample. Permeation through the tefzel is a function of chemical solubility in the tefzel, chemical

## Table 6
## Comparison of Tefzel Recoveries to Determine Temperature Effects on Tenax

| Target Compound | No Tube 25 °C | | Tefzel 25 °C | | Tefzel 70 °C | | Tefzel 100 °C | |
|---|---|---|---|---|---|---|---|---|
| | %R | | %R | | %R | | %R | |
| | T30 | BT[1] | T30 | BT | T30 | BT | T30 | BT |
| Trans-1,2-dichloroethene | 0 | 11 | 7 | 43 | 135 | 0 | 129 | 0 |
| Benzene | 98 | 0 | 107 | 0 | 127 | 0 | 126 | 0 |
| Trichloroethene | 96 | 0 | 101 | 0 | 119 | 0 | 129 | 0 |
| Toluene | 96 | 0 | 93 | 0 | 241 | 12 | 270 | 12 |
| Chlorobenzene | 98 | 0 | 85 | 0 | 115 | 0 | 131 | 0 |
| Ethylbenzene | 94 | 0 | 85 | 0 | 121 | 9 | 138 | 6 |
| Total Xylenes | 99 | 0 | 90 | 0 | 133 | 11 | 170 | 11 |

Note: Recoveries (%R) are based upon a 500-ng spike collected over a 30-min sampling period (T30) at a flow rate of 40 ml/min. Tefzel was permeable to contamination present in the oven.
[1] Breakthrough from first trap.

concentration gradient, and diffusivity through the polymer's intermolecular spaces. In the case of the contaminated oven, the steady state concentration of each compound was higher in the oven than in the tubing. Thus the direction of flow was from the oven, through the tubing, and into the gas stream. Higher temperatures increase the net mass transfer across a barrier by increasing the molecular energy of the chemical and by increasing the intermolecular spaces of the polymer. Larger intermolecular spaces allowed more permeant molecules to move through at faster rates. High temperatures also increased the solubility of the chemical in the tefzel. This type of permeation has been demonstrated for the Teflon fluoropolymers as well as for tefzel (Buxton, Goldsberry, and Henthorn 1993). Permeation could become important if heated tefzel were to be used as the transfer line. In one scenario, target analyte could be lost from the gas stream, resulting in low recoveries. In another, as was demonstrated here, contamination could become more important. In this case, the heat shrink forming the VOC sampler's umbilical as well as the inner wall of the push pipes must be relatively free of target analyte contamination for sampling results to be reliable.

Evaluation of the 1/16-in. stainless steel recoveries at different temperatures was more conclusive (Table 7). As was expected, the trans-1,2-dichloroethene recoveries in the first trap of every test were poor. The lowest recoveries occurred at the highest temperatures and flow rates. Clearly, analysis of this analyte and similarly volatile compounds requires a trapping medium suitable

**Table 7**
**Comparison of 1/16-in. Stainless Steel Recoveries to Determine Temperature Effects on Tenax**

| | No Tube 25 °C | | SS 25 °C | | SS 70 °C | | SS 100 °C | | SS 100 °C | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 40 ml/min | | 40 ml/min | | 40 ml/min | | 40 ml/min | | 60 ml/min | |
| | % R | | % R | | % R | | % R | | % R | |
| Target Compound | T30 | BT[1] | T30 | BT | T30 | BT | T30 | BT | T30 | BT |
| Trans-1,2-dichloroethene | 0 | 11 | 3 | 70 | 2 | 39 | 4 | 44 | 0 | 7 |
| Benzene | 98 | 0 | 106 | 0 | 98 | 0 | 101 | 0 | 106 | 0 |
| Trichloroethene | 96 | 0 | 105 | 0 | 98 | 0 | 99 | 0 | 101 | 0 |
| Toluene | 96 | 0 | 105 | 0 | 101 | 0 | 102 | 0 | 101 | 0 |
| Chlorobenzene | 98 | 0 | 96 | 0 | 96 | 0 | 97 | 0 | 101 | 0 |
| Ethylbenzene | 94 | 0 | 102 | 0 | 101 | 0 | 102 | 0 | 93 | 0 |
| m- and p-Xylenes | 100 | 0 | 97 | 0 | 97 | 1 | 100 | 0 | 108 | 0 |
| o-Xylene | 98 | 0 | 100 | 0 | 94 | 1 | 99 | 0 | 102 | 0 |
| m- and p-Dichlorobenzene | 100 | 0 | 91 | 2 | 85 | 8 | 96 | 4 | 105 | 0 |
| o-Dichlorobenzene | 103 | 0 | 93 | 0 | 80 | 0 | 88 | 0 | 94 | 0 |

Note: Recoveries are based on a 500-ng spike collected over a 30-min sampling period. Stainless steel (SS) was impermeable to contamination present in the oven.
[1] Breakthrough from first trap.

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for a wider range of volatile compounds. Recoveries of the dichlorobenzenes were the only significantly reduced recoveries through the stainless steel transfer line. When the gas flow was increased to 60 ml/min at a temperature of 100 °C, the recoveries remained above 90 percent. All breakthrough recoveries occurred for the less volatile xylenes and dichlorobenzenes and were less than 8 percent. Normal carry over within the GC/PID system may have contributed to some of these breakthrough concentrations.

Gas flowing through the test system may not have had sufficient time to heat because of the small internal volume of the 1/16-in. stainless steel transfer line. However, the temperature of the sampling port and trap external to the oven increased because of thermal conduction, but had no significant effect on analyte recovery.

Results from the 1/16-in. stainless steel breakthrough tests demonstrated that no significant analyte loss occurred because of tubing temperatures of 100 °C or a flow rate of 60 ml/min.

# VOC System Evaluation

### Probe fabrication contamination

Preliminary tests demonstrated that the VOC probe would require extensive cleaning before tests could proceed. Contamination appeared as cluttered chromatographic baselines and as significant concentrations of toluene and dichlorobenzene. Contamination came from two primary sources; oil and carbon residue remaining after the metal tooling and hardening processes, and from materials used to assemble the finished probe. Two solvents, hexane and methylene chloride, were used to remove machine oil from the disassembled probe. Although both solvents are relatively unresponsive to the PID (ie., have high ionization potentials), because of the large quantities of solvent and probe surface area, some signal was evident as the reassembled probe was purged and checked for contamination. Methylene chloride proved to be superior in removing oil and was relatively invisible to the PID detector. Hexane residues produced a stronger signal on the PID which, although it did not coelute with target analytes, may cause interferences if additional target compounds are added in the future. After the solvent wash, the pieces were dried in a vented oven at 100 °C for several hours to facilitate evaporation of solvents from the metal surfaces. Unhardened steel used in the prototype proved to be extremely porous to solvents. These probe components required more drying time to remove traces of solvents and contaminants than did the temperature-hardened components. All epoxies, resins, or solvents were tested for target compound contamination before the probe was reassembled. Resin-filled solder, solder flux, and flux remover contained high concentrations of toluene and were eliminated or heat treated after application to purge the toluene from the carrier gas path. A fluorocarbon-based compound (Krytox) was used to lubricate the O rings. Although this lubricant emits fluorocarbon compounds upon heating, these compounds are invisible to the PID detector. Krytox is thermally stable

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to a temperature of 260 °C, well above the desorption temperatures required by the VOC probe. However, since this is a fluorene-based lubricant, the standard safety practices such as use of gloves and adequate ventilation are recommended.

### Probe evaluation

Once the probe was demonstrated to be free of target analytes and background contamination, analyte recovery was tested. The sample chamber was sealed with an expanding plug, carrier gas flow was established, and the system checked for leaks. Initial tests isolated the effects of the probe alone on analyte recovery by placing the tenax trap directly on line 4, the probe's sample exit port (see Figure 5). Table 8 compares recovery from tests performed under two sets of conditions. In the first, carrier gas flow was 40 ml/min with a sample chamber temperature of 70 °C. In the second, the gas flow was increased to 60 ml/min and the temperature was increased to 100 °C. The resulting data show no substantial difference; therefore, either set of conditions would be acceptable in a leak-free system.

**Table 8**
**Comparison of Recovery From Probe at Different Flows and Temperatures**

| Target Compound | % R 40 ml/min Flow Rate 70 °C | % R 60 ml/min Flow Rate 100 °C |
|---|---|---|
| Trans-1,2-dichloroethene | 13.6 | 5.7 |
| Benzene | 108 | 101 |
| Trichloroethene | 102 | 98.6 |
| Toluene | 96.4 | 99.1 |
| Chlorobenzene | 95.0 | 94.3 |
| Ethylbenzene | 99.0 | 96.7 |
| m- and p-Xylenes | 98.2 | 98.8 |
| o-Xylene | 100 | 102 |
| m- and p-Dichlorobenzene | 88.6 | 91.3 |
| o-Dichlorobenzene | 85.8 | 87.4 |

Note: No tubing was used. Recoveries are based on a 500-ng spike and a sampling time of 30 min.

Comparisons of recoveries with each of the three types of tubing at different temperatures showed that tefzel demonstrates the poorest recoveries (Table 9). With the tubing at ambient temperature (25 °C), all of the

**Table 9**
**Comparison of Recoveries From Tefzel Tubing Attached to Probe**

| Target Compound | No Tube 25 °C<br>% R | Tefzel 25 °C<br>% R | Tefzel 70 °C<br>% R |
|---|---|---|---|
| Trans-1,2-dichloroethene | 5.7 | 48.5 | 67.7 |
| Benzene | 101 | 61.8 | 76.9 |
| Trichloroethene | 98.6 | 49.1 | 77.3 |
| Toluene | 99.1 | 38.3 | 61.2 |
| Chlorobenzene | 94.3 | 9.2 | 51.0 |
| Ethylbenzene | 96.7 | 26.8 | 65.5 |
| *m*- and *p*-Xylenes | 98.8 | 17.4 | 63.8 |
| *o*-Xylene | 102 | 20.6 | 64.4 |
| *m*- and *p*-Dichlorobenzene | 91.3 | 1.7 | 17.1 |
| *o*-Dichlorobenzene | 87.4 | 5.0 | 35.8 |

Note: All recoveries are based upon a 500-ng spike collected over a 30-min period. Flow rates were 60 ml/min, and probe sample chamber temperatures were 100 °C. Breakthrough at T30 was not collected.

compounds were recovered at less than 50 percent. An increase in tube temperature to 70 °C improved recoveries to a mean of approximately 70 percent. As was expected, dichlorobenzene recoveries were the poorest in both cases. Surprisingly, the addition of the probe to the system improved recoveries of the volatile trans-1,2-dichloroethene.

Recoveries for the 40 ml/min, 70 °C control and the 100 °C test, in a gas-tight system with the stainless steel tube/probe, were excellent for all compounds except for the trans-1,2-dichloroethene (Table 10). With the exception of *o*-dichlorobenzene (88.4 percent), all recoveries were above 95 percent.

The PEEK tubing also yielded good recoveries (>90 percent) for the target analytes (Table 11). Lower recoveries (<90 percent) were observed for the dichlorobenzenes as was demonstrated in the initial tube evaluation (Table 4). Clearly, PEEK and 1/16-in. stainless steel tubing are preferable to the tefzel in terms of analyte recovery.

## Effects of soil type

Vicksburg loess, a standard silt, at 10-percent moisture (10-percent silt) was used to evaluate recovery from a spiked soil. In a preliminary test using an unheated tefzel transfer line and a sample chamber temperature of 70 °C, water

**Table 10**
**Comparison of Recoveries From 1/16-in. Stainless Steel Tubing Attached to Probe**

| Target Compound | No Tube 25 °C | SS 25 °C | SS 70 °C |
|---|---|---|---|
| | | Probe Temperature | |
| | 70 °C | 100 °C | 100 °C |
| | % R | % R | % R |
| Trans-1,2-dichloroethene | 13.6 | 0.0 | 3.0 |
| Benzene | 108 | 105 | 111 |
| Trichloroethene | 102 | 105 | 108 |
| Toluene | 96.4 | 104 | 108 |
| Chlorobenzene | 95.0 | 97.1 | 97.4 |
| Ethylbenzene | 99.0 | 105 | 107 |
| m- and p-Xylenes | 98.2 | 96.4 | 98.0 |
| o-Xylene | 100 | 102 | 100 |
| m- and p-Dichlorobenzene | 88.6 | 95.2 | 100 |
| o-Dichlorobenzene | 85.8 | 88.4 | 97.5 |

Note: Recoveries are based upon a 500-ng spike collected on tenax traps over a 30-min period at a flow rate of 40 ml/min.

**Table 11**
**Comparison of Recoveries From PEEK Tubing Attached to Probe**

| Target Compound | No Tube 25 °C | PEEK 25 °C | PEEK 70 °C |
|---|---|---|---|
| | % R | % R | % R |
| Trans-1,2-dichloroethene | 5.7 | 28.6 | 56.1 |
| Benzene | 101 | 107 | 110 |
| Trichloroethene | 98.6 | 101 | 104 |
| Toluene | 99.1 | 107 | 102 |
| Chlorobenzene | 94.3 | 96.0 | 90.9 |
| Ethylbenzene | 96.7 | 101 | 92.4 |
| m- and p-Xylenes | 98.8 | 102 | 99.0 |
| o-Xylene | 102 | 102 | 97.1 |
| m- and p-Dichlorobenzene | 91.3 | 76.8 | 83.3 |
| o-Dichlorobenzene | 87.4 | 90.4 | 87.8 |

Note: All recoveries are based upon a 500-ng spike collected on tenax traps over a 30-min period at a flow rate of 60 ml/min. Sample chamber temperatures were 100 °C. Breakthrough at T30 was not collected.

condensed and collected in the tubing. Transfer line temperatures were adjusted upward to 70 °C and finally to 100 °C in an attempt to keep the water in the vapor state until it reached the cooler (25 °C) tenax trap. Since water vaporized and moved into the transfer line at the lower sample chamber temperatures, that temperature was also raised to 100 °C. This allowed drying of the soil as thoroughly and as quickly as possible and minimized sampling time. By the end of the 2-hr sample collection period, water droplets were observed dripping from the end of the final trap (T120).

A major concern was the effect of soil moisture on the tenax trapping media and the analytical system. Tenax cartridges have been used for direct sampling and analysis of water for trace organic compounds including toluene, chlorobenzene, ethylbenzene, total xylenes, and o- and p-dichlorobenzene (Pankow et al. 1988). Analyte recoveries greater than 90 percent demonstrate tenax's excellent sorption capabilities under saturated conditions. Recoveries within the VOC sampler system might be reduced, however, if condensed water prevented the target analytes from contacting the tenax. In addition, water retained in the trap could interfere with GC analysis. The latter was found to be the more serious problem to overcome. Water vapor that is purged from the tenax trap during analysis by GC/PID elutes from the analytical column at the same temperatures as the first four analytes, trans-1,2-dichloroethene, benzene, TCE, and toluene. As a result, response from these compounds is substantially reduced or quenched, resulting in a complete loss of those compounds for that sample. Pankow et al. (1988) dried tenax cartridges using a two-step centrifugation and vacuum desiccation process before desorbing directly into a GC/MS. A more simplified drying process was used for the VOC sampler system. Traps were dried at ambient temperature with helium at a flow rate of 40 ml/min for 30 min. To test the effects of drying on analytes trapped on the tenax, traps were spiked directly, omitting the transfer line, with 1,000 ng of analyte. Half of the traps were analyzed immediately without any drying step, and half were purged with helium before analysis. Water vapor was not present in the test system. Results show no significant losses of analyte because of this drying process (Table 12). Each trap was dried in this manner when removed from the VOC sampler system during soil tests, enabling data to be collected on all target analytes.

In tests to compare recoveries from spiked silt using the three types of tubing as transfer lines, stainless steel yielded the highest recoveries of TCE and BTEX compounds and also displayed the lowest residual contamination in the tubing (T60 data) (Table 13). The T30 values from the stainless steel tubing with the spiked silt soil compared favorably with recovery data from the probe with no soil present (Table 10). Tefzel tubing substantially lowered recoveries from the soil spike and retained the most analyte.

The silt soil experiments showed that 1/16-in. stainless steel tubing was the best overall choice from a chemical standpoint. Therefore, the soil evaluation was completed using this tubing. Limitations resulting from its small inner diameter can be corrected by system redesign.

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**Table 12**
**Comparison of Traps Dried to Reduce Water-Quenching Problem on GC/PID**

| Target Compound | Traps Not Dried | | Traps Dried | |
|---|---|---|---|---|
| | % R | (SE) | % R | (SE) |
| Trans-1,2-dichloroethene | 1.0 | 0.3 | 25.1 | 24.2 |
| Benzene | 98.0 | 1.2 | 97.5 | 1.3 |
| Trichloroethene | 103 | 3.8 | 99.8 | 5.7 |
| Toluene | 99.9 | 0.6 | 100 | 0.5 |
| Chlorobenzene | 96.1 | 2.1 | 97.8 | 1.3 |
| Ethylbenzene | 94.5 | 0.7 | 97.8 | 2.4 |
| m- and p-Xylenes | 96.8 | 1.6 | 97.7 | 1.7 |
| o-Xylene | 105 | 2.0 | 101 | 0.1 |
| m- and p-Dichlorobenzene | 98.4 | 2.2 | 96.0 | 3.0 |
| o-Dichlorobenzene | 99.8 | 2.2 | 95.1 | 5.0 |

Note:  Recoveries (standard error) are based on a 1,000-ng spike and a sampling time of 30 min.  Drying was 30 min with helium at a flow of 40 ml/min at 25 °C.

**Table 13**
**Comparison of Recoveries From Silt With a Moisture Content of 10 Percent**

| Target Compound | Tefzel | | PEEK | | Stainless Steel | |
|---|---|---|---|---|---|---|
| | T30 | T60 | T30 | T60 | T30 | T60 |
| | % R (SE) | % R (SE) | % R (SE) | % R (SE) | % R (SE) | % R (SE) |
| Trans-1,2-dichloroethene | 40.0 (30.8) | 1.3 (0.3) | 23.6 (0.6) | 0.2 (0.2) | 0.0 (0.0) | 0.2 (0.2) |
| Benzene | 49.0 (1.4) | 4.1 (0.1) | 91.3 (6.8) | 1.1 (1.1) | 96.5 (2.0) | 0.3 (0.1) |
| Trichloroethene | 85.8 (12.9) | 5.6 (1.6) | 90.5 (5.2) | 0.9 (0.9) | 93.4 (1.2) | 0.0 (0.0) |
| Toluene | 33.6 (1.0) | 5.1 (0.8) | 95.7 (4.0) | 1.0 (1.0) | 102 (2.8) | 0.5 (0.1) |
| Chlorobenzene | 28.5 (2.0) | 3.7 (0.5) | 89.4 (2.6) | 1.0 (1.0) | 95.7 (1.0) | 0.6 (0.1) |
| Ethylbenzene | 33.1 (5.7) | 2.8 (0.3) | 91.6 (3.8) | 0.7 (0.7) | 92.9 (1.2) | 0.6 (0.1) |
| m- and p-Xylenes | 29.5 (6.1) | 3.4 (0.2) | 99.0 (1.5) | 0.9 (0.9) | 101 (1.3) | 0.9 (0.2) |
| o-Xylene | 36.8 (3.0) | 5.6 (1.4) | 72.4 (20.2) | 0.9 (0.9) | 100 (1.3) | 0.6 (0.1) |
| m- and p-Dichlorobenzene | 19.4 (3.4) | 8.2 (1.6) | 81.4 (0.8) | 2.9 (2.9) | 93.1 (2.1) | 1.7 (0.5) |
| o-Dichlorobenzene | 25.7 (4.0) | 6.6 (1.7) | 99.7 (6.9) | 3.5 (3.5) | 125 (8.2) | 2.2 (0.4) |

Note:  Probe temperature was set at 100 °C with a flow of 60 ml/min (stainless steel - 40 ml/min). Tube temperature was 100 °C.  Sampling time was 30 min with soil in chamber (T30) and 30 min after soil was ejected from chamber (T60).

Analyte recovery was significantly lower in the silt soil at 20-percent mois-
ture and in the clay soil ((P < .05) compounds indicated by * in Table 14).
Soil analysis showed that from 1 to 7 percent of analyte remained in the soil
following 30 min of thermal desorption in the VOC sampler (Table 15). In
addition, these two soils had lower drying efficiencies (Table 17). These data
indicate that recovery of BTEX compounds will be reduced in soils with high
clay or high moisture contents. This can be due to incomplete volatilization of
analyte from the soil sample or to solubilization and retention of analyte in
water condensing within the system. Additionally, water coating the tenax
could form a barrier inhibiting adsorption of gaseous analyte during its brief
residence time within the trap. However, even the reduced recoveries from the
VOC sampler soil comparison tests were generally greater than 80 percent.

## Table 14
## Comparison of Recoveries From Different Soil Types and Two Different Moisture Contents

| Target Compound | Silt 10% M<br>% R (SE) | Silt 20% M<br>% R (SE) | Sand 10% M<br>% R (SE) | Clay 10% M<br>% R (SE) | Mean % Rec<br>% R (SD) | 8240[1]<br>% R (SD) |
|---|---|---|---|---|---|---|
| Trans-1,2-dichloroethene | 0.0 (0.0) | 1.4 (0.2) | 2.7 (0.6) | 1.8 (0.6) | 1.5 (1.1) | -- |
| Benzene | 96.5 (2.0) | 69.3* (0.8) | 92.6 (2.1) | 87.8 (2.0) | 86.6 (12.1) | 101 (7) |
| Trichloroethene | 93.4 (1.2) | 89.5 (2.5) | 86.8 (1.6) | 77.7 (7.3) | 86.9 (6.7) | 102 (7) |
| Toluene | 102 (2.8) | 94.1 (2.9) | 95.9 (1.0) | 88.3 (1.3) | 95.0 (5.4) | 102 (6) |
| Chlorobenzene | 95.7 (1.0) | 87.8 (3.2) | 92.3 (0.1) | 81.7* (0.3) | 89.4 (6.1) | 101 (4) |
| Ethylbenzene | 92.9 (1.2) | 93.9 (1.9) | 91.2 (2.9) | 81.7* (0.3) | 89.9 (5.6) | -- |
| m- and p-Xylenes | 101 (1.3) | 90.5 (4.2) | 96.8 (0.7) | 90.0 (1.0) | 94.6 (5.4) | -- |
| o-Xylene | 100 (1.3) | 89.0* (1.0) | 96.3 (0.6) | 86.8* (0.5) | 93.2 (6.4) | -- |
| m- and p-Dichlorobenzene | 93.1 (2.1) | 81.3 (3.8) | 86.5 (0.7) | 79.1 (2.9) | 85.0 (6.2) | — |
| o-Dichlorobenzene | 125 (8.2) | 88.2 (1.8) | 108 (10.3) | 98.7 (7.4) | 105 (15.6) | -- |

Note: Tubing was 1/16-in. stainless steel heated to 100 °C. Probe temperature was 100 °C with a flow rate of
40 ml/min.
[1] Mean and standard deviation were calculated from matrix spike recoveries using USEPA SW-846 Method 8240 by
GC/MS.
* Compounds exhibiting mean values dissimilar to the other treatments.

## Estimated target compound recoveries

Treatment recoveries for all three soils were averaged and the standard
deviations calculated and compared with laboratory-generated means and stan-
dard deviations of the four compounds used as matrix spikes for USEPA
Method 8240 (Table 14). Considering the differences in sampling and han-
dling, the mean VOC sampler recoveries compare very favorably with
Method 8240 GC/MS recoveries.

**Table 15**
**Soil Residue After a 30-min Sampling Period at 100 °C With a Flow Rate of 40 ml/min**

| Target Compound | Silt 10% M | Silt 20% M | Sand 10% M | Clay 10% M |
|---|---|---|---|---|
| | % R | % R | % R | % R |
| Trans-1,2-dichloroethene | -- | 1 | -- | -- |
| Benzene | -- | 5 | -- | -- |
| Trichloroethene | -- | -- | -- | -- |
| Toluene | 1 | 4 | -- | 1 |
| Chlorobenzene | -- | 7 | -- | -- |
| Ethylbenzene | -- | 2 | -- | -- |
| Total Xylenes | -- | 6 | -- | -- |

Note: Analysis was by USEPA Method 8240 using GC/MS. Data were obtained from one replicate per soil type.

## Estimated carryover between samples

The mean percentages of analyte residues remaining in the VOC sampler system after the soil had been sampled for 30 min then ejected were estimated from the T60 and T120 data (Tables 14 and 15). These data represent the estimated percentage of sample that could be carried over into the next sample from a 1,000-ng spike (Table 16). Trans-1,2-dichloroethene was omitted because no valid data were obtained from the tests. By adding a 30-min heated purge of the sample chamber and transfer line, the T60 carryover could be purged from the system. The T120 data represent an additional hour of purging. The VOC sampler carryover was obtained by multiplying the standard deviation of the T120 data by 3. This is an estimate of the maximum amount that the sample residue could contribute to carryover into the next sample. In addition, the GC manufacturer predicts a 1- to 2-percent carryover between samples with concentrations greater than 200 µg/ℓ by purge and trap. When summed, these two values yield an estimate of the total maximum percentage carryover expected for a soil in that concentration range (Table 16). These values are an estimate of the VOC system's practical quantitation limit (PQL). For a soil with concentrations of toluene at 200 ng/g (200 ppb), the total expected carry-over would be 4 percent or 8 ng/g. For comparison, the PQL for the GC/PID is approximately 5 ng/g (5 ppb) in soil.

## Mechanical functions

Once inside the probe, the soil was successfully and efficiently purged of volatile compounds. However, another important issue to be determined was

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**Table 16**
**Estimated Residue Carryover Between Samples Calculated From 1/16-in. Stainless Steel T60 and T120 Data Expressed in Percent**

| Target Compound | Mean T60 | | Mean T120 | | VOC Sampler | GC | Total Estimate | GC |
|---|---|---|---|---|---|---|---|---|
| | % R | (SE) | % R | (SE) | Carryover % | Carryover % | Carryover % | PQL ng/g |
| Trans-1,2-dichloroethene | – | – | – | – | – | 2.0 | ~ 2 | 5 |
| Benzene | 0.8 | (0.3) | 0.1 | (0.1) | 0.6 | 2.0 | 2.6 | 5 |
| Trichloroethene | 0.9 | (0.5) | 0.4 | (0.3) | 2.3 | 2.0 | 4.3 | 5 |
| Toluene | 1.5 | (0.6) | 1.0 | (0.2) | 2.0 | 2.0 | 4.0 | 5 |
| Chlorobenzene | 0.9 | (0.1) | 0.8 | (0.2) | 1.5 | 2.0 | 3.5 | 5 |
| Ethylbenzene | 0.8 | (0.1) | 0.7 | (0.2) | 1.4 | 2.0 | 3.4 | 5 |
| m- and p-Xylenes | 1.2 | (0.2) | 1.0 | (0.2) | 1.4 | 2.0 | 3.4 | 5 |
| o-Xylene | 1.5 | (0.3) | 0.9 | (0.2) | 2.0 | 2.0 | 4.0 | 5 |
| m- and p-Dichlorobenzene | 2.3 | (0.5) | 1.6 | (0.3) | 2.5 | 2.0 | 4.5 | 5 |
| o-Dichlorobenzene | 3.2 | (0.7) | 2.2 | (0.4) | 3.2 | 2.0 | 5.2 | 5 |

Note: The VOC sampler carryover is calculated as 3X the standard deviation of the T120 data. It is expressed in percent and is based upon spikes of 1,000 ng.

**Table 17**
**Soil Moisture and Sample Volume Data**

| Soils | Soil Moisture (a) | Dried Plug (b) | Difference (c) | Drying Efficiency | Soil Plug, g |
|---|---|---|---|---|---|
| | Mean % (SE) | Mean % (SE) | % | % | Mean Wt. (SE) |
| Silt (10% M) | 9.2 (0.07) | 0.3 (0.15) | 8.9 | 96.7 | 6.3 (0.52) |
| Sand (10% M) | 7.0 (0) | 0.2 (0.15) | 6.8 | 97.1 | 7.1 ( 0.25) |
| Clay (10% M)[1] | 11.5 (0.70) | 1.1 (0.80) | 11.1 | 91.0 | 6.6 (0.75) |
| Silt (20% M) | 16.2 (0.15) | 9.2 (0.25) | 7.0 | 43.2 | 11.8 (0.43) |

Note: Drying efficiency was calculated as a ratio of the percent moisture lost during the sampling process ((c/a) × 100).
[1] Clay replicates were taken from different batches and had slightly different initial percent moistures.

whether the mechanical design would function as planned and withstand repeated operation. Mechanical functions include the internal workings of the probe, temperature control, soil drying efficiency, soil removal, and control of gas flows.

As stated earlier, O rings seal the spaces between the steel cylinders into gas-tight chambers. Gas enters the probe via three transfer lines. To save space and minimize the size of the probe, these gas flows perform more than one function. Two of these lines drive the piston attached to the actuator rod. As the piston is forced up, the gas must also force the locking lugs to release. The third line delivers the carrier gas to the sample chamber after first sweeping over the entire outer surface of the actuator rod housing. This area also contains the electrical connections for the heater and thermocouple. Any form

of contamination on this surface is swept into the sample chamber with the carrier gas. In addition, when the actuator rod is forced down to seal the probe, the carrier gas must also pressurize the outer housing chamber sufficiently to force the locking lugs into place to secure the probe tip.

Some of the O rings failed when the actuator rod was tested, generally a result of damage occurring during assembly. To reduce failure and increase O ring life, the inner walls of the probe were honed and polished. Krytox lubricant was also liberally applied to the O rings upon assembly.

Heat, moisture, and dried soil can reduce O ring effectiveness in the sample chamber area. These O rings must be cleaned and lubricated after the probe is withdrawn from the ground and may need to be replaced before the VOC sampler is reused. Gas flow rates or system pressure should be monitored to determine the status of the O ring seals during sampling. Future probe designs will reevaluate the placement of each of these seals to minimize system leaks.

Temperatures were observed to vary a few degrees from the heater to the center of the sample chamber and also along the length of the heater surface, depending upon the density of the wire wrap. The thermocouple, attached to one side between the ceramic and the stainless steel, monitors temperature at one point on the heater surface. When activated, the heater comes to temperature within 30 min and maintains temperature readings ±5 °C. During one phase of testing, the heater operated continuously for 3 weeks without problems. Immediately after soil was pushed into the sample chamber, the temperature dropped 8 to 10 °C, but returned to the set point within 10 to 15 min as the soil dried and was purged of volatiles. Soils with more moisture or more capacity to retain moisture took longer to dry. After the soil was ejected, the temperature quickly increased as much as 25 °C inside the sample chamber. This occurred because the chamber was no longer sealed and the carrier gas could no longer transfer heat efficiently. Between pushes, the temperature must be regulated by either reducing the voltage or by continuing the carrier gas flow at all times.

During the course of the evaluation, the VOC probe was redesigned to strengthen the heater system and to improve its soil ejection capabilities. After sampling, the soil must be ejected from the chamber to allow the chamber to be closed and pushed to a new sampling depth. Tests showed that, with the exception of sand, the soil sample dried intact as a cylindrical plug. Occasionally, the plug tilted slightly to one side. Occasionally, if the soil was overpushed, the plug bulged and became larger in diameter than the chamber opening, preventing ejection. Normally, however, the soil plug remained undistorted. The primary means of soil removal was by pressurizing the sample chamber and forcing the soil plug out of the bottom. For this to happen, the seal between the cutting edge of the probe and the bottom of the plug could not be broken. During tests in which contact with the reservoir of moist soil was not broken, the soil ejected easily after 30 min of drying. The interior, bottom wall of the sample chamber is sloped toward the opening to facilitate soil removal. Gentle movement of the actuator rod, if possible, might also

help break up any larger pieces of dried soil. Action of the rod alone did not successfully remove any of the intact plugs. Instead, the soil was packed around the bottom of the chamber, halting any further downward movement and preventing the probe tip from sealing.

Since the sample chamber depth is 4.45 cm from the cutting edge to the actuator rod tip retracted inside the chamber, the push must be controlled so that no more than 4.45 cm of soil enters the sample chamber. Overpushing will force soil up into the space around the probe tip and into the four sample exit ports, blocking gas flow. If reversed-flow gas pressure cannot clear the sampler, the probe may have to be withdrawn from the ground to clean the ports. While the stainless steel protective sleeve was added to the inside of the ceramic heater, a severe overpush could destroy the heater and sample chamber.

### Drying efficiencies and soil sample volumes

Average initial moisture contents for the 20-percent silt, 10-percent silt, sand, and clay were 16.2, 9.2, 7.0, and 12.2 percent, respectively (Table 17). After 30 min in the sample chamber at 100 °C, the 10-percent silt and sand were reduced to less than 0.5 percent, while the clay retained an average of 1.0-percent moisture. The 20-percent silt retained the most moisture, 9.2 percent. Drying efficiencies (the ratio of water lost compared with the original moisture content) ranged from 43 to 97 percent. Water removal from the sample chamber was incomplete for the 20-percent silt. This may have been because the soil plug weights (11.8 g) were nearly double the weights for the other soils. When removed from the sample chamber, these sample plugs were slightly distorted indicating an overpush. Water beads were observed clinging above and around the tip of the actuator rod when the cone tip was unscrewed to remove the soil from the sample chamber. However, T60 and T120 system residue measurements from the 20-percent silt were not significantly different from the other three treatments. This suggests that spike compound was moving efficiently out of the system as it was purged.

The probe is designed to cut a 4.76-cm$^3$ plug of soil when pushed to a depth of 4.45 cm. Using a weight density of 1.7 g/cm$^3$, the soil sample should weigh a maximum of 8.1 g. Soil samples were estimated to average from 6 to 7 g. The effective volume of the soil exposed to heat and carrier gas flow is 3.54 cm$^3$, which is equivalent to 6 g. If an average effective soil volume is assigned, the concentration of the target compounds can be estimated in terms of volume (i.e., micrograms/milliliters or milligrams/liter). If the soil density is known, the concentration can be estimated in terms of wet mass.

## GC/PID Capabilities

Overall, the GC system was relatively easy to learn and use. GC/PID/ ELCD is normally used to selectively detect the BTEX compounds at low

nanograms/liter concentrations. The SRI GC/PID evaluated has a PQL of 5 µg/ℓ, which is roughly equivalent to 5 ng/g (5 ppb) in soil. The calibration curve was sigmoidal with an operating range from 1 to 500 µg/ℓ. As the PID lamp ages, the upper limit for the BTEX compounds and chlorobenzene may drop to 200 µg/ℓ.

In normal purge and trap analysis, one trap is used for the standard and all the samples. Traps usually last for months or hundreds of samples. For this evaluation, many traps were used and their positions in the analytical scheme were rotated. After 5- to 6-months use, some of the traps used for these tests suffered significant reduction of sorptive capabilities. Expected analyte retention times shifted in some and, in others, recoveries fell off sharply. All traps should, therefore, be evaluated before use and their performance monitored on a regular basis. It may be best to choose one trap as the standard while rotating the others. Traps should be discarded when sorption capacity falls 20 percent.

Low-detection limits and a low-operating range may be a drawback if hotspots are sampled. While action or cleanup levels set by States for BTEX-contaminated soils may be in the low ppm range, concentrations at contaminated sites could vary up to percentage ranges. If a trap containing excessively high concentrations of compound is unknowingly purged into the GC, the detector will overload; the tubing could become so contaminated that the entire fluid system might have to be replaced. To protect the system, prior knowledge of the contaminant plume is essential to avoid the more highly contaminated areas.

If high concentration samples are taken, methanol can be used to elute compound from the tenax. To demonstrate this, a trap was spiked directly with 2,500 ng of standard. The trap was eluted with three aliquots of methanol totaling 1 ml. A portion of the methanol (up to 0.1 ml) was added to the purge water and analyzed as a diluted water sample. Recoveries confirmed that the extraction method was feasible (Table 18). However, these traps may not be reusable because methanol behaves similarly to water in the PID by suppressing signal from the first four eluting compounds.

## Carrier Gas Supply Manifold

Figure 5 has a schematic of the manifold used to control carrier gas supply to the VOC sampler. The manifold was constructed from stainless steel fittings, tefzel tubing, and electric switching valves. Carrier gas supplied from one cylinder was routed through the manifold to perform all of the probe functions. Before tests started, the sample carrier gas route was trapped and found to be free of contamination. Mechanically, the manifold functioned satisfactorily.

**Table 18**
**Recoveries From a Trap Extracted With Methanol to Evaluate an Alternate Method for Analyzing High-Level Samples**

| Target Compound | Final Concentration, ng | Final Recovery, % |
|---|---|---|
| Trans-1,2-dichloroethene | 150 | 6.0 |
| Benzene | 2,460 | 98.4 |
| Trichloroethene | 2,490 | 97.8 |
| Toluene | 2,510 | 100 |
| Chlorobenzene | 2,420 | 96.8 |
| Ethylbenzene | 2,585 | 103 |
| *m*- and *p*-Xylenes | 4,505 | 90.1 |
| *o*-Xylene | 2,205 | 88.2 |
| *m*- and *p*-Dichlorobenzene | 4,685 | 93.7 |
| *o*-Dichlorobenzene | 2,275 | 91.0 |

Note: The trap was spiked with 2,500 ng of each compound.

# 4   Conclusions

No one sample tubing fulfilled all of the selection criteria.  Tests showed that 1/16-in. stainless steel tubing consistently gave the best recoveries (>91 percent) and had the lowest contamination levels.  Moreover, the slight lack of flexibility in the stainless steel tubing is countered by the combined weight and rigidity of the umbilical.  If the probe can successfully be redesigned to eject the soil, stainless steel is the best choice for the sample tubing.

Heated tubing is needed to transfer water vapor and target compounds to the surface.  Maximum recoveries were achieved within 30 min for the compounds tested.  Probe and tube conditions were 100 °C with a flow rate of 40 to 60 ml/min.  If less volatile compounds are added to the target analyte list, the temperatures may need to be raised to prevent condensation along the transfer line.  Baseline detection limits were established for the combined VOC sampler and GC system at 5 ppb with an average estimated analyte carryover of 4 percent.

Complete system tests yielded recoveries greater than 85 percent from soil spiked with BTEX and other chlorinated volatile compounds.  These recoveries compared favorably with spike recovery data obtained from USEPA Method 8240 for GC/MS.  Recoveries of four compounds (benzene, chlorobenzene, ethylbenzene, and o-xylene) differed by soil type and moisture content.  Silt at 20-percent moisture and clay showed the greatest difference.  These differences may be characteristic of thermal desorption and not unique to the VOC sampler system.  At a desorption temperature of 100 °C, the sampler was capable of effectively drying soils with moisture contents up to 17 percent.  Mean drying efficiencies were 95 percent for the three soils at 10-percent moisture and 43 percent for the 20-percent silt.  Samples with higher moisture content retained traces of compound in the soil after a 30-min sampling period.

Mechanical functioning tests revealed several design weaknesses.  The present design can expose carrier sample gas to fabrication and assembly contamination.  Critical O rings can fail after repeated use and will need to be checked and replaced after the probe is removed from each sampling hole.  In addition, the probe was not always able to eject the soil and close after sampling.  Probe redesign, however, should be able to resolve these problems.

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Overall, the laboratory evaluation demonstrated that the VOC sampler works. The VOC sampler successfully desorbed volatile target analytes from uniform, spiked laboratory soil and transported them efficiently through 50 ft of heated 1/16-in. stainless steel tubing into a tenax trap where they were analyzed by GC/PID. Overall recoveries were greater than 85 percent.

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# Appendix A
# Tube Manufacturing Contamination Evaluation—Tentatively Identified Compounds

**Table A1**
**Control for Tubing Manufacturing Contamination**

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 589388 | 3-Hexanone | 14.83 | 4.8 J | 45 |
| 95501 | 1,2-Dichlorobenzene | 15.71 | 9.7 J | |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of injection port sampled for 1 hr. RT = retention time; Q = goodness of fit; and J = estimated concentration below instrument detection limit.

## Table A2
## Viton Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 355373 | 1,1,1,2,2,3,3,4,4,5,5,6,6, tridecafluorohexane | 4.08 | 110.0 | 90 |
| 123728 | Butanal | 6.64 | 89.0 | 91 |
| 110623 | Pentanal | 8.98 | 180.0 | 38 |
| 2213232 | 2,4-Dimethyl heptane | 10.52 | 29.0 | 53 |
| 66251 | Hexanal | 11.43 | 350.0 | 80 |
| 110430 | 2-Heptanone | 13.62 | 47.0 | 87 |
| 111717 | Heptonal | 13.78 | 210.0 | 42 |
| 582241 | 2-Hydroxy-1-phenyl ethanone | 15.26 | 230.0 | 50 |
| 124130 | Octanal | 15.52 | 240.0 | 86 |
| 95501 | 1,2-Dichlorobenzene | 15.70 | 85.0 | 97 |
| 17312606 | 6-ethyl-undecane | 16.26 | 120.0 | 78 |
| 124196 | Nonanal | 16.93 | 200.0 | 83 |
| 112403 | Dodecane | 17.66 | 60.0 | 86 |
| 628615 | 2-Chlorooctane | 18.51 | 70.0 | 43 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

## Table A3
## Nylon Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 110543 | Hexane | 6.03 | 16.0 J | 90 |
| 123728 | Butanal | 6.64 | 21.0 J | 90 |
|  | m- and p-Dichlorobenzene | 15.70 | 19.0 J | 91 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

## Table A4
## Glass Capillary Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 95501 | 1,2-Dichlorobenzene | 15.71 | 20.0 J | 91 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

## Table A5
## Teflon Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 111659 | Octane | 14.83 | 26.0 | 78 |
|  | m- and p-Dichlorobenzene | 15.71 | 100.0 | 96 |
| 1120214 | Undecane | 16.27 | 27.0 | B6 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

## Table A6
## Tefzel Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 40723635 | 1,1,2,2,tetrafluoropropane | 2.87 | 670.0 | 43 |
|  | unknown | 3.69 | 4,400.0 | 0 |
| 35262545 | 1,1,1,2,2,5,5,6,6-nonafluorooctane | 4.02 | 750.0 | 36 |
| 648362 | 3,3,4,4-tetrafluorohexane | 4.40 | 590.0 | 12 |
| 136367 | unknown | 6.65 | 2,700.0 | 0 |
| 7227910 | unknown | 7.29 | 560.0 | 0 |
| 35262545 | 1,1,1,2,2,5,5,6,6-nonafluorooctane | 8.19 | 1,200.0 | 33 |
|  | unknown | 10.09 | 2,500.0 | 0 |
| 35278796 | 1,1,1,2,2,5,5,6,6,9,9,10,10-decane | 11.27 | 520.0 | 16 |
| 40723691 | 3,3,4,4,7,7,8,8,-octafluorodecane | 13.42 | 390.0 | 56 |
| 35262545 | 1,1,1,2,2,5,5,6,6-nonafluorooctane | 14.70 | 1,900.0 | 64 |
| 31163845 | 3-methyl-1-nitropyrazole | 15.83 | 920.0 | 42 |
| 35262545 | 1,1,1,2,2,5,5,6,6,-nonafluorooctane | 16.29 | 340.0 | 72 |
| 35262545 | 1,1,1,2,2,5,5,6,6-nonafluorooctane | 16.61 | 480.0 | 59 |
| 425321 | 1,1'-(1,1,2,2,-tetrafluorobenzene) | 17.14 | 350.0 | 35 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

### Table A7
### Stainless Steel (1/16-in.) Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| | *m*- and *p*-Dichlorobenzene | 15.70 | 32.2 | 97 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

### Table A8
### Nickel SP Alloy Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 110543 | Hexane | 7.13 | 28.8 | 90 |
| | *m*- and *p*-Dichlorobenzene | 12.41 | 17.9 J | 93 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

### Table A9
### PEEK Manufacturing Contamination

| CAS Number | Compound Name | RT, min | Estimated Concentration, ng | Q |
|---|---|---|---|---|
| 1191964 | unknown hydrocarbon | 4.22 | 14.0 | 0 |
| 592416 | 1-hexene | 5.94 | 13.0 | 90 |
| 123728 | Butanal | 6.65 | 19.0 | 72 |
| 2452995 | 1,2-dimethyl-cyclopentane | 8.06 | 4.3 | 90 |
| 2213232 | 2,4-dimethyl heptane | 10.53 | 15.0 | 64 |
| 66251 | Hexanal | 11.43 | 17.0 | 90 |
| 120923 | Cyclopentanone | 11.65 | 7.8 | 74 |
| 17301325 | 4,7-dimethyl undecane | 12.89 | 18.0 | 42 |
| 111717 | Heptanal | 13.78 | 16.0 | 53 |
| 108941 | Cyclohexanone | 14.11 | 15.0 | 90 |
| 124185 | Decane | 14.84 | 29.0 | 40 |
| 24070777 | Cyclopentanol | 15.53 | 21.0 | 43 |
| 541731 | Dichlorobenzene | 15.71 | 50.0 | 96 |

Note: Tentatively identified compounds (TICs) from GC/MS analysis (Method 8240) of tubing heated to 70 °C and sampled for 1 hr.

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**13. ABSTRACT (Maximum 200 words)**

Conventional subsurface contaminant mapping technology requiring borings and laboratory analysis of soil samples is time-consuming, expensive, and often results in inadequate descriptions of contaminant plumes. Adaptation of advanced chemical techniques to cone penetrometer technology provides a means for real time detection and mapping of contamination in the subsurface. An in situ volatile organic compound sampling system to detect ppb levels of BTEX compounds (benzene, toluene, ethylbenzene, and total xylenes) and trichloroethene has been developed for the site characterization and analysis penetrometer system. The sampler is pushed to a desired depth in the subsurface, an interior actuator rod is retracted to form a sampling chamber, and a measured volume of soil is sampled and purged in place. Volatilized compounds are transferred to the surface where they are trapped on tenax and desorbed into a portable gas chromatograph. The soil sample is expelled, and the penetrometer is pushed to a new depth where the process is repeated.

Materials and system-operating conditions were optimized during laboratory tests. Stainless steel tubing heated to 100 °C and a carrier gas flow rate of 40 ml per min yielded maximum recoveries (>90 percent) in a 30-min sampling period. Complete system tests yielded recoveries greater than 85 percent from soil spiked with BTEX and
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other chlorinated volatile compounds.  These recoveries compared favorably with spike recovery data obtained from U.S. Environmental Protection Agency Method 8240 by gas chromatograph/mass spectrometer.

Overall, the sampling system was able to successfully thermally desorb BTEX compounds from spiked soil and transport the volatilized compounds through 50 ft of heated transfer line into a tenax trap with recoveries greater than 85 percent.